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March 1956

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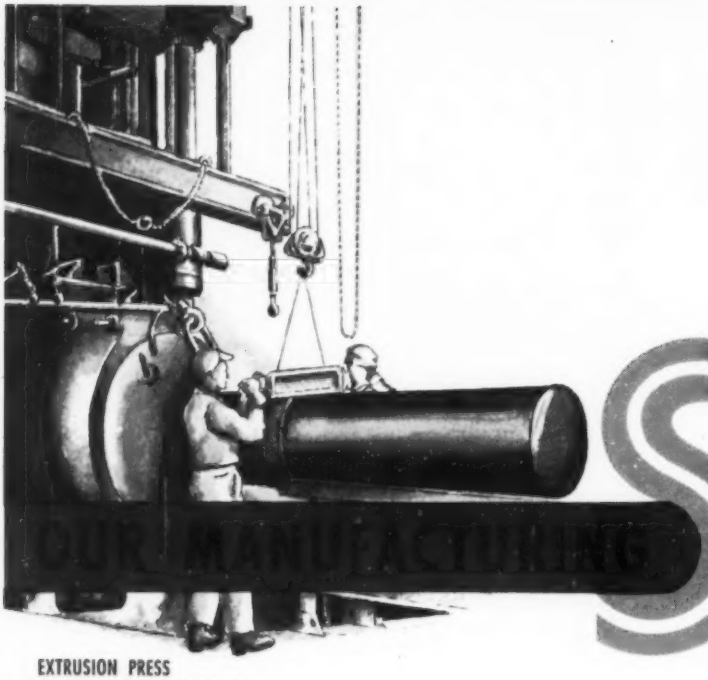

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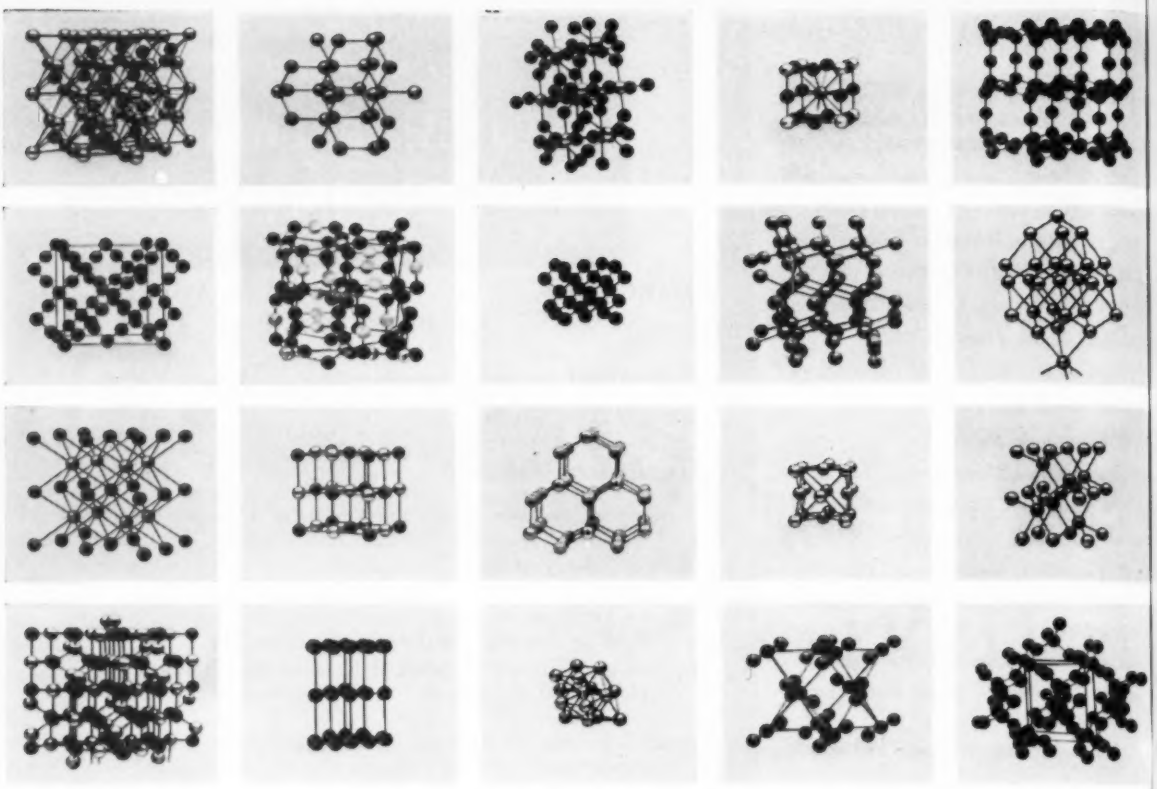

Crystal structure models. Top row, left to right: cuprite, zincblende, rutile, perovskite, tridymite. Second row: cristobalite, potassium dihydrogen phosphate, diamond, pyrites, arsenic. Third row: caesium chloride, sodium chloride, wurtzite, copper, niccolite. Fourth row: spinel, graphite, beryllium, carbon dioxide, alpha-quartz.

FROM ATOMS TO STARS

Research at Bell Telephone Laboratories ranges from the ultimate structure of solids to the radio signals from outer space. Radio interference research created the new science of radio astronomy; research in solids produced the transistor and the Bell Solar Battery.

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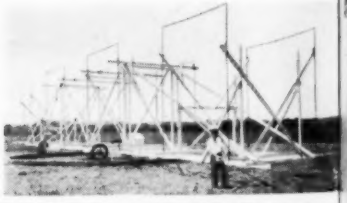
Models of the atomic patterns in solids help Bell Laboratories scientists visualize their electrical behavior.



Directional antenna used by Karl G. Jansk in discovery of stellar radio signals at Be Telephone Laboratories in 1932.

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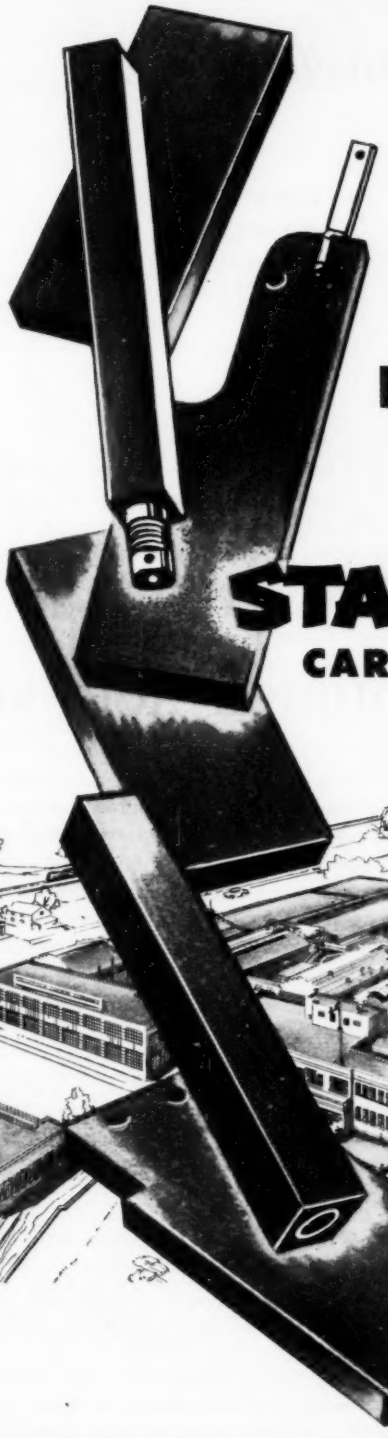

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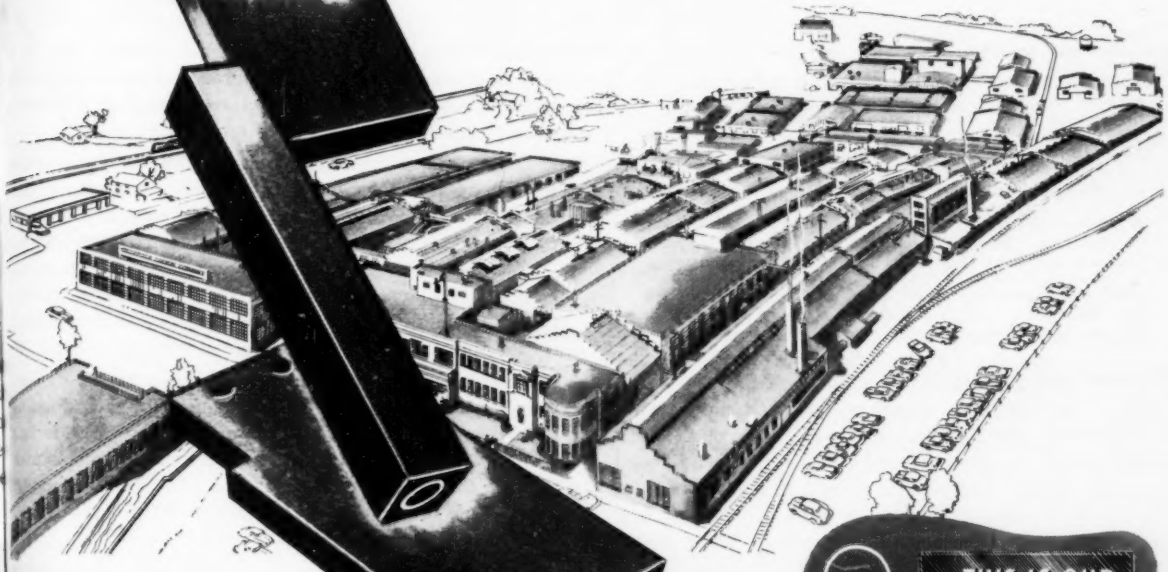

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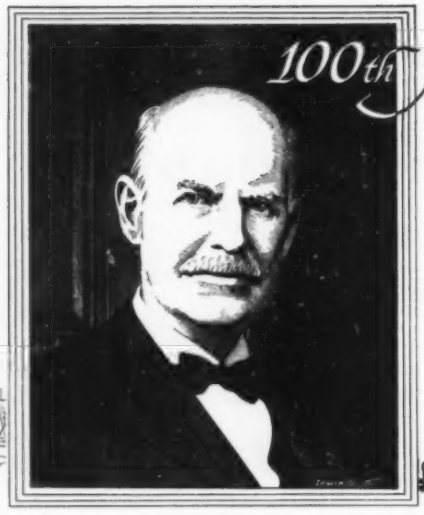

100th Anniversary

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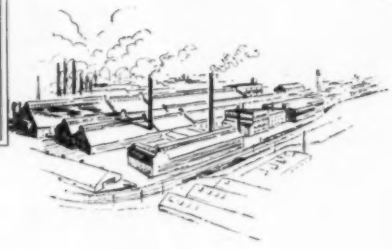

this was genius . . .

EDWARD GOODRICH ACHESON

Yes, this was genius.

Thomas A. Edison knew it. In paying tribute upon the occasion of Doctor Acheson's passing, he said "... as a former associate I know the world loses a great genius."

Leo Hendrik Baekeland knew it. He remembered him "as a man who combined a most fertile brain with great strength of conviction."

Walter B. Pitkin knew it. This famous psychologist said "As he created his place in our civilization so does that place pass with him. No one shall fill it."

And the press knew it. They used in their editorials such phrases as "world's acclaim of a genius," "one of the geniuses of his time," and "the loss of an inventive genius."

But what makes genius?

Employing a mixture of carbon, sand, salt, and sawdust in a simple but effective electric furnace, made up of a few strands of wire, a carbon rod, and a plumber's bowl, Edward Goodrich Acheson was able to bring into being a mass of scintillating crystals rivaling many gems in splendor and almost matching the diamond in hardness. These highly abrasive crystals he crushed and made into grinding wheels, and these wheels, in turn, were used to shape metals and make machines. Called "Carborundum" by Acheson and silicon carbide by the chemist, this new material did its job so well that it is credited with making possible today the mass production of automobiles, tractors, and countless other mechanisms.

Possibly silicon carbide could be made better—harder or sharper. To this end Acheson subjected silicon carbide to higher temperatures for longer periods; what he obtained was not a harder substance but, instead, one of the softest—pure graphite. The extreme conditions to which he had exposed his jewels of industry brought about their disintegration, the silicon passing off as vapor and the carbon remaining as a soft, unctuous residue. Manufactured graphite, destined to be of far-reaching importance, became another of Acheson's contributions to industry.

Unquenchable curiosity, coupled with the indomitable spirit that was his, led him to uncover means of preparing this new product of the electric furnace in the form of plates and cylinders. Put to work as electrodes, these soon revolutionized electrochemical and electrometallurgical operations. Acheson had now made commercially feasible the production of new families of chemicals and laid the groundwork for the present efficient manufacture of steel and alloys.

During Acheson's painstaking efforts to produce graphite crucibles he experimented with many clays for use as binding agents—and he learned much about them—so much in fact that he was able to explain why the ancient Egyptians used straw in their brick making and what caused the formation of the deltas of the Nile and Mississippi. Most important, he discovered a method of rendering graphite colloidal.

Colloidal graphite in modern industry plays a role that is varied and complex, its unique properties finding utility in such dissimilar fields as lubrication, electronics, metalworking, and lithography, to name a few. The techniques originated by Acheson for colloidally dispersing graphite are being applied to other solids including carbon blacks, pigments, and minerals.

To those of us in the companies identified with Doctor Acheson, his perseverance and achievement are an inspiration. We are proud to offer this tribute to his genius on the 100th anniversary of his birth.

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Editorial

Edward Goodrich Acheson

EDWARD GOODRICH ACHESON was a Charter Member of The Electrochemical Society. He was born just 100 years ago, on March 9, 1856, in Washington, Pa. Having had to earn his own living from the age of 16, he had no formal higher schooling. Nevertheless, he found it possible to become a well-read, successful scientist-inventor and an educated, cultured man. His death in 1931 was mourned by a host of personal friends, by the electrochemical industry, and by the general public as well.

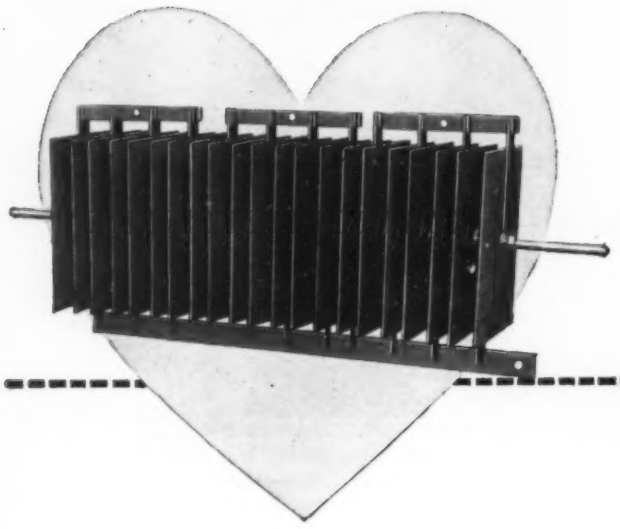
Acheson was an avid reader and experimenter in the field of science from the moment he realized that such opportunities existed; he liked electrical experimentation especially. At one time he was employed as a laborer by Thomas A. Edison; later he became Edison's assistant. However, he preferred to work independently when finances permitted. He was intrigued by invention, and during his lifetime acquired some 70 U. S. patents. Many of these were for equipment and processes now obsolete, but some of his discoveries and inventions have contributed immeasurably to the well-being, comfort, and luxury of civilized man, and will continue to do so indefinitely.

Acheson is best known for his contributions to the development of the electric furnace as a large-scale industrial tool, his discovery of "carborundum" and methods of making it economically, his finding that graphite superior to the natural product could be made cheaply in the electric furnace, and his preparations Oildag and Aquadag ("Deflocculated Acheson Graphite" in suitable colloidal suspensions). As is true of many inventions, there was an element of accident in the initial production of carborundum and graphite; but it was no accident that Acheson was hard at work on well-conceived plans, or that his keen eyes and mind did not overlook anything potentially useful in his experiments.

Carborundum is an abrasive which has aided in no small measure the tremendous advances in machine construction in the past 50 years. It is very hard, but, unlike diamond for example, is sufficiently brittle to be crushed easily to any desired particle size. It can be used for hard grinding, final honing, polishing the most delicate jade. Acheson graphite, on the other hand, is so useful partly because, unlike natural graphite, it is almost completely nonabrasive. It can be used as a dry lubricant, or in the "dags" as required. In addition it can be made in, or machined into, almost any desired size or shape. Nowadays it can be made practically free of neutron-absorbing impurities.

Acheson's genius, industry, and contributions to the welfare of society were well recognized during his lifetime, and he was the recipient of numerous medals, awards, and public honors. In 1928 he provided The Electrochemical Society with funds for the award each two years of the Edward Goodrich Acheson Medal. In 1929 he became the first recipient of the Medal. This was, of course, none of his doing; the award was made by the Society, which had no more worthy candidate for the honor. Since that time 12 additional Acheson Medals have been awarded to distinguished electrochemists, and the 14th award will be made at the Cleveland Meeting of the Society in October of this year. The Medalists are doubly honored by having the name of Edward Goodrich Acheson head their list.

—CVK



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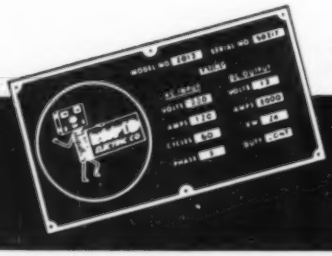

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Resistivity Studies of Various Leclanché Cathode Materials

RICHARD GLICKSMAN AND C. K. MOREHOUSE

RCA Laboratories, Radio Corporation of America, Princeton, New Jersey

ABSTRACT

It has been suggested that there is a correlation between dry cell performance and resistivity of various manganese dioxides. Resistivity data obtained on four types of manganese dioxides over a range of applied pressures up to 100,000 lb/in.^{2} (7.03×10^6 g/cm^2) show quite different resistivity vs. applied pressure relationships. These differences, however, are minimized by blending high resistivity manganese dioxide with low resistivity acetylene black and electrolyte, and it is concluded that resistivity of manganese dioxide cannot have an appreciable effect on the performance of a dry cell.

INTRODUCTION

The importance of the manganese dioxide electrode of the Leclanché-type dry cell and the variation in performance between cells containing manganese dioxide materials of different crystallographic forms has prompted a number of questions as to the electrical properties of manganese dioxide.

In this paper, resistivity data at various applied pressures and apparent densities of dry cell components, including acetylene black, various types of manganese dioxides, and mixtures of each, are presented. This study was made to determine whether a correlation in cell performance with resistivity of cathode materials could be made.

EXPERIMENTAL APPARATUS

The apparatus used for measuring resistivities is shown in Fig. 1. It consists essentially of a pair of steel electrodes (approximately 1½ in. diameter and 1 in. long) with arms 1^{11}⁄$_{32}$ in. long and ¼ in. diameter. These arms fit closely into a plastic liner (natural paper base tubing,[1] ¼ in. I.D.) which was placed in a steel cylinder for support. A small sample (0.1–0.5 g) of the material to be measured was placed between the ends of the electrodes inside the plastic tubing and compressed successively from 1,250 to 100,000 lb/in.^{2} (8.79×10^4 to 7.03×10^6 g/cm^2) by applying pressure to the ends of the electrode by means of a hydraulic press.

Resistance and volume measurements were made at various applied pressures. The resistance of the powder was measured with a Leeds & Northrup Type S-2 portable Wheatstone bridge (0.1% accuracy). All measurements were corrected for the resistance of the steel electrodes and connecting wires (0.033 ohm). The volume occupied by the sample at various pressures was determined from a knowledge of the cross-sectional area which is defined by the I.D. of the tubing, and by the difference between the known length of the electrodes and the measured length with the sample between the electrodes. Resistivity (ohm-cm) and apparent density (g/cc) were calculated for each pressure.

[1] Obtained from the Synthane Corp., Oaks, Pa.

ELECTRICAL RESISTIVITY DATA FOR ACETYLENE BLACK[2]

Acetylene black is an important constituent of dry cells and is blended with the highly resistant manganese dioxide cathode to provide an electrode of low resistance. Benson, Gluck, and Kaufmann (1) measured the resistivity of acetylene black over a pressure range of 100–2000 lb/in.^{2} ($7.0 \times 10^3 - 1.4 \times 10^5$ g/cm^2). Extending this work, resistivity data obtained on 0.1 g samples of acetylene black, 50% compressed, over a pressure range of 1,250–100,000 lb/in.^{2} ($8.79 \times 10^4 - 7.03 \times 10^6$ g/cm^2) are presented in this paper.

The measured resistivity values for acetylene black, plotted against apparent density and applied pressure are shown in Fig. 2 and 3. Each point on the curves represents the average of three different samples, with the individual measurements deviating from the mean no more than 5%. Also shown are results for an acetylene black, 100% compressed, reported by Benson and co-workers as sample B in Table II of their paper. Their results reported in ohm-in.[3] were converted to ohm-cm.

Benson, Gluck, and Kaufmann (1) and Sweitzer and Goodrich (3) found that in comparing the resistivity of carbon blacks of widely different properties, standard pressure could not be used as the only basis, and that values at equal apparent densities gave more comparable results, which is in accord with the findings of this work.

It is possible to compare the two sets of data over only a limited range of apparent densities, since much higher pressures were applied in the present study. For an apparent density of 0.70 g/cc, Benson and co-workers measured a resistivity of 0.086 ohm-cm as compared with the value of 0.061 ohm-cm found by the present authors. Benson (4) reported a resistivity of 0.076 ohm-cm at a density of 0.70 g/cc for both 50 and 100% compressed acetylene black. Thus, there is a reasonable agreement between the two sets of data.

In Fig. 2 and 3 it is seen that the resistivity approaches a constant value of 0.010 ohm-cm at pressures of approximately 30,000–40,000 lb/in.^{2} ($2.1–2.8 \times 10^6$ g/cm^2) and

[2] Material obtained from Shawinigan Chemicals Ltd., Shawinigan Falls, Que., Canada.

[3] In the original publication the results were erroneously printed as ohm/in. instead of ohm-in. (2).

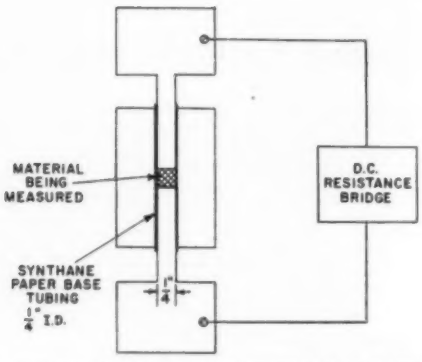

FIG. 1. Apparatus for measuring resistivity of powdered materials.

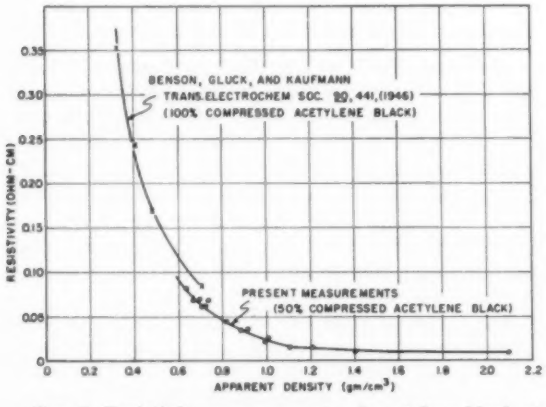

FIG. 2. Resistivity measurements of acetylene black at various apparent densities.

at an apparent density of approximately 1.2 g/cc. Thus contact resistance between particles ceases to become a variable at pressures and apparent densities above these values.

ELECTRICAL RESISTIVITY DATA FOR VARIOUS MANGANESE DIOXIDES

A survey of the literature shows that resistivity values of manganese dioxide ranging from 100 to 10^6 ohm-cm have been reported (5–7); however, these values have not been carefully identified with respect to the physical and chemical properties of the material. Fox (8) more recently investigated the effects of hot pressing various manganese dioxides, and prepared materials with a density of 2.0–2.7 g/cc which have a resistivity of less than 100 ohm-cm.[4]

Resistivity data were gathered on four different types of manganese dioxides which are characterized by the chemical and physical data shown in Table I and Fig. 4. Manganese dioxide, type A, was made by the thermal decomposition of manganese nitrate. Type B was prepared by anodic deposition on graphite from a hot sulfuric acid solution of manganous sulfate. Type C manganese dioxide was prepared by treating a reduced African manganese dioxide material with sulfuric acid. The manganese dioxide which settled out was filtered and washed free of acid.

[4] These results were reported as ohms/cc.

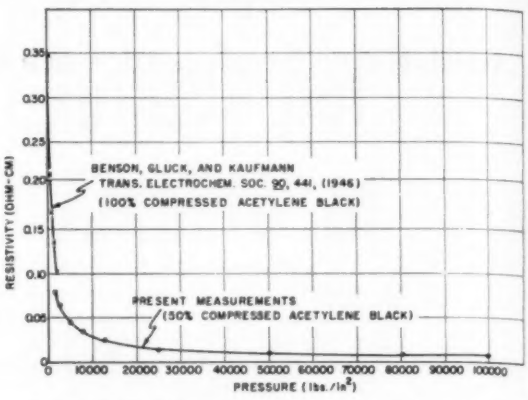

FIG. 3. Resistivity measurements of acetylene black at various applied pressures.

Type D was naturally occurring African Gold Coast manganese dioxide. Data presented in Fig. 5 and 6 represent the average of two different 0.5 g samples, with the individual measurements deviating from the mean by less than 10%. These results were obtained by the same technique as described for measuring the resistivities of acetylene black.

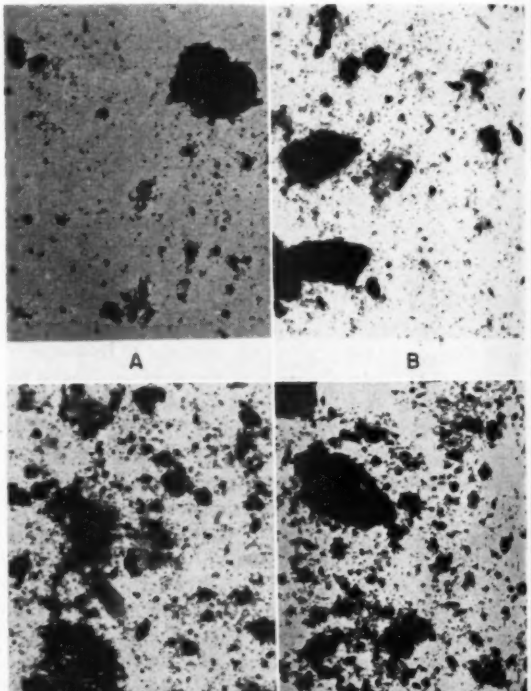

FIG. 4. Electron micrographs of various types of manganese dioxide: (*A*) from thermal decomposition of $Mn(NO_3)_2$; (*B*) produced electrolytically; (*C*) produced by chemical treatment of African ore; (*D*) naturally occurring African ore. (10,000× before reduction for publication.)

TABLE I. *Various properties of manganese dioxide materials*

Classification	A		B		C		D	
Method of preparation	Thermal decomposition of $Mn(NO_3)_2$		Anodic deposition on graphite electrodes from aqueous solution of H_2SO_4 and $MnSO_4$		Chemically treated African ore		Naturally occurring African Gold Coast	
% MnO_2	84.6		85.0		85.0		84–85	
% Total Mn	58.1		59.0		59.0		58.0	
Apparent density	0.70 g/cc (11.5 g/in.^{3})		1.28 g/cc (21.0 g/in.^{3})		1.12 g/cc (18.5 g/in.^{3})		1.37 g/cc (22.5 g/in.^{3})	
	X-ray diffraction patterns							
	d	I/I_1	*d*	I/I_1	*d*	I/I_1	*d*	I/I_1
	7.312	12	7.107	16	5.046	11.4	4.045	35.4
	5.842	15.7	4.085	23.2	4.005	14	3.376	13.6
	3.890	26.2	2.433	28.9	3.376	22	3.142	24.7
	3.491	19.1	2.337	100	3.142	40	2.587	12.6
	3.142	10.4	2.131	14.9	2.419	100	2.419	63
	2.742	11.8	2.036	18.9	2.337	93.5	2.337	100
	2.405	63.5	1.635	33.3	2.153	29.4	2.153	28.4
	2.350	100	1.438	7.1	2.109	29.4	2.036	25
	2.142	2	1.395	11.9	2.036	22.3	1.896	13.5
	2.036	57	1.221	3.9	1.845	17.9	1.829	13.6
	1.914	7.2	1.174	4.9	1.628	79.2	1.635	59
	1.628	4	1.061	4.2	1.561	22.3	1.567	8.4
	1.521	12			1.544	28	1.428	17.4
	1.468	8.5			1.428	46.4	1.363	19.4
	1.428	18.7			1.385	22.7	1.304	14.4
	1.395	4.3			1.304	22.3	1.221	8.4
	1.346	18.2			1.223	15.3	1.168	5
	1.304	8.5			1.058	5	1.069	9.1
	1.218	8.5			0.9996	8.9		
	1.063	6.7						
	0.9121	8.5						

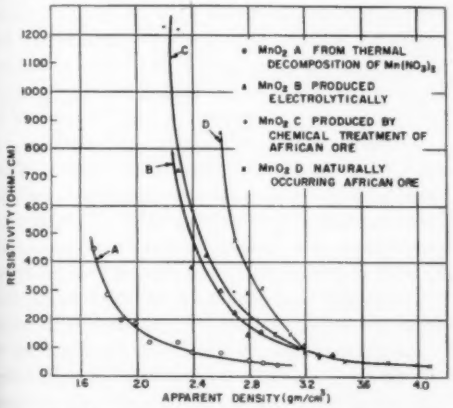
MnO2 A FROM THERMAL DECOMPOSITION OF Mn(NO3)2
MnO2 B PRODUCED ELECTROLYTICALLY
MnO2 C PRODUCED BY CHEMICAL TREATMENT OF AFRICAN ORE
MnO2 D NATURALLY OCCURRING AFRICAN ORE
RESISTIVITY (OHM-CM)
APPARENT DENSITY (gm/cm3)

FIG. 5. Resistivity measurements of different manganese dioxides at various apparent densities.

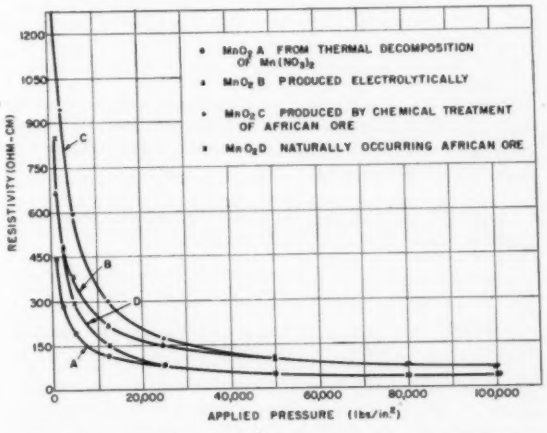
MnO2 A FROM THERMAL DECOMPOSITION OF Mn(NO3)2
MnO2 B PRODUCED ELECTROLYTICALLY
MnO2 C PRODUCED BY CHEMICAL TREATMENT OF AFRICAN ORE
MnO2 D NATURALLY OCCURRING AFRICAN ORE
RESISTIVITY (OHM-CM)
APPLIED PRESSURE (lbs/in2)

FIG. 6. Resistivity measurements of different manganese dioxides at various applied pressures.

The data show that as the pressure on the sample or the apparent density is increased, all four samples approached resistivity values between 37–77 ohm-cm at about 100,000 lb/in.^{2} (7.03×10^6 g/cm^2) or at 3.0–3.4 g/cc. Thus it appears that at these high pressures and densities, the contact resistance between the particles is practically eliminated, and the specific electrical resistivity of the material is approached.

At equal apparent densities, before the materials reached their lowest resistivity, material A had lower resistivity value than the other three manganese dioxides. It might be thus surmised that the contact resistance between particles of material A was lower than that between particles of the other three materials. From x-ray diffraction and electron micrograph data, it is seen that the structure and particle size distribution is different in all four of these materials. Material A appears to have a larger number of smaller particles than the others, and it is believed that the difference in resistivity of the four

manganese dioxides is due to differences in particle size and structure of the materials. Since manganese dioxide is a semiconductor, variation in impurities might also account for these differences.

Since there is an obvious difference between the resistivity curves of the four materials as the applied pressure is varied, an attempt was made to correlate the resistivity data with manganese dioxide performance, both in polarization studies and in actual cells.

If the manganese dioxides are rated on the basis of lowest resistivity at a given apparent density, it is found that the lower the resistivity of the sample, the greater is the capacity in amp-min/g (9). The results are reported in Table II, where the rating of four manganese dioxides is given both on a weight and volume basis, along with other data.

TABLE II. *Rating of various types of manganese dioxides**

Classification of manganese dioxide	Method of preparation	Scotts density (g/in.³)	Polarization studies		Signal Corps data** capacity (hr)
			Capacity (amp-min/g)	(amp-min/in.³)	
A	Thermal decomposition of $Mn(NO_3)_2$	11.5	6.6–8.8	76–101	6.4
B	Electrolytic deposition	21.0	5.3	111	6.5–7.5
C	Chemically treated African ore	18.5	2.6–3.0	48–56	4.5–5.0
D	Naturally occurring African ore	22.5	1.1–1.9	25–43	4

* Ref. (9).

** "A" size Leclanché cells discharged continuously through a 16⅔ ohm resistance to 1.00 v per cell. Data supplied by Power Sources Branch of the Signal Corps Engineering Laboratories.

TABLE III. *Resistivities in ohm-cm of various materials, both pure and when mixed with acetylene black, at various pressures*

Material	Pressure (lb/in.²)			
	40,000 (2.8×10^6)*	60,000 (4.2×10^6)*	80,000 (5.6×10^6)*	100,000 (7.0×10^6)*
MnO_2 C	120	96.0	81.0	67.7
10–1 MnO_2 C—black mix	0.87	0.67	0.60	0.54
MnO_2 D	60.0	50.0	47.8	40.0
10–1 MnO_2 D—black mix	0.70	0.61	0.52	0.48
Sulfur	$>10^9$	$>10^9$	$>10^9$	$>10^9$
10:1 sulfur—black mix	2.11	1.81	1.69	1.59
Acetylene black	0.012	0.009	0.009	0.008

* Values in parenthesis are in g/cm².

Making the same comparison of resistivity with capacity in amp-min/in.³, and in actual cells, the ratings of the two best manganese dioxides are (materials A and B) reversed. This would be expected in view of the low density of material A compared with that of B, as found by Scotts density method (10). Material A would therefore give less capacity in an actual dry cell than material B, since the capacity of a dry cell is dependent on the amount of material in the cell, as well as its activity per unit weight.

From the above data it might be inferred that a correlation between resistivity and the capacity of manganese dioxides in dry cells exists. However, before any conclusions can be drawn from the data, it is necessary to clear up two important points: first, the effect of blending the manganese dioxides with acetylene black on the resistivity of the mixture, since such a mixture constitutes the cathode of a dry cell; second, the over-all effect of the internal resistance on cell performance.

Resistivity measurements of mixtures of ten parts manganese dioxide to one part acetylene black are shown in Table III for materials C and D. Additional measurements were made of similar sulfur-acetylene black mixtures for comparison. The results are reported at the higher pressures in order to minimize resistivity differences resulting from contact resistance. At these high pressures, the uncertainty involved in measuring small changes in apparent density is large, so resistivities are given at equal applied pressures.

As shown in Table III, the bulk resistivity of manganese dioxide is about 10^4 times that of acetylene black. Conduction through mixtures containing one part acetylene black and ten parts manganese dioxide, therefore, is predominantly through chains of the very low resistivity acetylene black particles. Resistivities of such mixtures are little affected by substituting manganese dioxides with different resistivities. Even when sulfur, with a resistivity greater than 10^9 ohm-cm, is substituted for manganese dioxide, with a resistivity of approximately 100 ohm-cm, the resistivity of the mixture is increased by a factor of only three. The small effect of resistivity differences of various manganese dioxides is further decreased in conventional dry cells, wherein the cathode material has been mixed not only with acetylene black, but also with a highly conducting electrolyte. It is concluded that the resistivity of the manganese dioxide is of little importance in determining the internal resistance of a dry cell. Furthermore, the internal resistance of a dry cell is initially low and changes very little during discharge (11) so the resistivity of manganese dioxide is not an important factor in eventual cell failure.

In view of the above, no correlation can be made between the resistivity of a manganese dioxide and its performance in a cell. That there does appear to be a correlation stems from the fact that the differences in resistivity values of the manganese dioxides can be accounted for by differences in particle size and structure. These differences can also influence cell performance, as has been shown by other investigators.

Acknowledgment

The authors wish to thank the Power Sources Branch of the Signal Corps Engineering Laboratories for making

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Anodic Film Growth on Hafnium in Nitric Acid

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ABSTRACT

In 70% nitric acid at room temperature, an anodic film developed uniformly over single hafnium crystals with a thickness dependent upon the metal crystal orientation. At 0.025 ma/cm² the cell voltage did not exceed 1.5 v. At 1.5 ma/cm² the cell voltage rose to 185 v and the film was broken down by sparking. In each case, the anodizing produced more oxide on metal crystal planes which had shown greater oxide growth on zirconium under similar conditions. At 90°C and 0.025 ma/cm², the oxide developed discontinuously over single hafnium crystals with the formation of wedge-like patches. The degree to which these patches covered the grains was not related to the metal crystal face in the same way as the thickness of the room temperature film. The discontinuous growth was attributed to nucleation at metal surface imperfections. An orientation effect in the electropolishing of hafnium was also noted.

INTRODUCTION

Many metals which can be anodized develop a film whose thickness is proportional to the cell voltage (1). This behavior has been shown to apply to zirconium (2) and was indicated for hafnium (3). Also, in the case of zirconium, a steady growth of oxide occurs at a low and steady cell voltage (3). This was designated as "low-resistance" oxide to distinguish it from the oxide whose thickness was proportional to cell voltage (designated "high-resistance"). The rate of formation of the low-resistance oxide was found to be dependent on the orientation of the underlying metal crystal (4) as well as on current density and on concentration of nitric acid.

In the case of hafnium, a high-resistance film, similar to the film on tantalum (3), occurred at 1 ma/cm². Evidence for the low-resistance type of oxide has now been obtained and is presented here. Both high- and low-resistance films were found to be influenced by the metal orientation. Nucleation effects were indicated in the latter case.

EXPERIMENTAL

A large-grained hafnium specimen was cleaned by polishing and etching. It was then anodized in 70% nitric acid at 0.025 and at 1.5 ma/cm², room temperature, and at 0.025 ma/cm², 90°C. The specimen consisted of a cross section of hafnium crystal bar which was machined to a disk 0.45 cm thick × 3.0 cm diameter. The original wire used in production could be seen in the center of the disk. The specimen was chosen because of its large grains (containing marked substructure). Spectrographic analysis of the turnings showed the following composition in weight per cent: Zr, 3; Ti, 0.3; As, Ba, Ca, Mo, P, V, Zn, less than 0.1; Ag, Al, B, Be, Bi, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sb, Si, Sn, less than 0.01. A tantalum rod was screwed to the rim of the disk when anodizing. The tantalum was insulated from the electrolyte by anodizing to 240 v direct current in dilute KOH before insertion into the hafnium. Wet grinding consisted of polishing to 400 grit paper on a wheel with flowing water. A solution of HF and HNO_3 [1] was used for etching, followed by an immediate hot tap water rinse. Electropolishing was done in a mixture of acetic and perchloric acids[2] cooled with tap water. All photomicrographs were taken with bright field illumination. Orientations of the underlying metal grains were determined after anodizing by the back-reflection Laue technique.

[1] 8 ml conc. hydrofluoric acid (48%), 50 ml conc. nitric acid (70%), 50 ml hot tap water.

[2] 100 ml conc. perchloric acid (70%), 1000 ml glacial acetic acid.

FIG. 1. Appearance of a section of hafnium crystal bar after anodizing at 1 ma/cm² in 70% nitric acid 3 hr at room temperature.

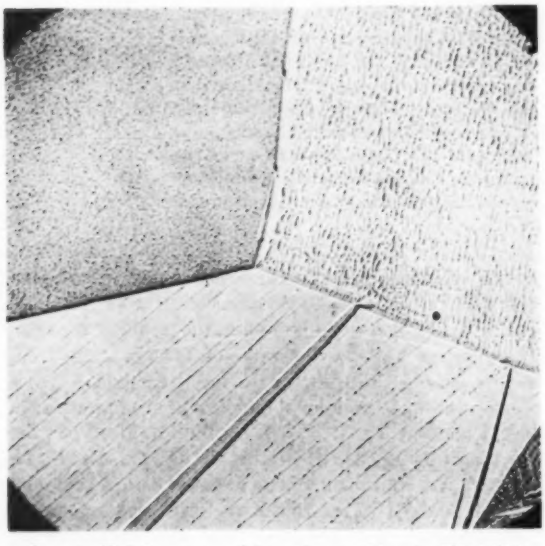

FIG. 2. Hafnium crystal bar after etching in HF-HNO_3. 500× before reduction for publication.

RESULTS

Anodizing with High Film Resistance

The specimen was first studied under conditions which produce a high-resistance film. These were 1.5 ma/cm² and room temperature. At this current density, the surface developed interference colors which varied from grain to grain. At 170 v a play of sparks began on the surface and the clear interference colors began to disappear until a dull gray surface resulted. Each of the extremely fine sparks caused a localized destruction of the oxide layer.

TABLE I. *Orientation and appearance of 8 grains on hafnium crystal bar after various surface treatments*

Degrees from (001)	Appearance after anodizing 0.025 ma/cm²		Nature of furrow-like structure after electropolishing
	Room temperature	90°C	
34	Dark*	Solid to nearly solid black	Random
50	Dark*	Variable, from no black to scattered black areas	Random
50	Dark*	Solid black	Random
68	Dark*	Very light brown, no black oxide	Oriented†
68	Dark*	Very fine scattered black areas distributed in a parallel reticulated pattern	Oriented†
83	Light	No black	None
87	Light	Nearly solid black	None
88	Light	Scattered to solid black	None

* Color differences were not sufficiently distinctive to be useful.

† These grains showed an interference grating effect.

The sparks were short-lived at first but persisted longer as the anodizing continued and became fewer in number. They were also observed to spread out in a circle of increasing diameter until a grain boundary or previously sparked area was encountered. As the line of sparks advanced, the surface was observed to change sharply from a clear blue or green color to dull gray.

The sparking produced more oxide on some grains than on others. When anodizing was prolonged beyond the voltage maximum (185 v) for a total of 3 hr at 1.5 ma/cm² (room temperature), the result shown in Fig. 1 was obtained. In this photograph the white areas consist of a relatively thick friable layer of HfO_2 [3] and the other areas are dull gray. A quantitative estimate of the amount of oxide produced was not made. The grains in the foreground show a difference in oxide thickness in orthogonal directions.

Laue back-reflection patterns were obtained from two of the hafnium metal grains, one of which had a gray surface and the other a white surface. For this purpose, the friable oxide was removed by scraping.

The plane of anodizing of the hafnium grain which had a white surface was close to (1126), 27° from the basal plane. The plane of anodizing of the grain with a gray surface was close to (3123), 60° from the basal plane. The former plane was also preferentially anodized in the case of zirconium (4), suggesting a similarity in anodic mechanism.

Anodizing with Low Film Resistance

The specimen was next studied under two conditions selected to produce a low-resistance film. These were: 0.025 ma/cm², 25°C and 0.025 ma/cm², 90°C. The results of these treatments are described below. In consideration of the surface changes which occurred, an area of particular interest on the specimen is shown in Fig. 2 (as etched).

[3] Monoclinic HfO_2 as determined by x-ray powder pattern.

The anodizing characteristics of the three contacting grains were very different as indicated in successive figures. These particular grains were too small for convenient determination of their orientation.

Anodizing at 0.025 ma/cm², 25°C.—Preliminary anodizing of the hafnium disk overnight at 0.025 ma/cm² produced a film with thicknesses dependent on the underlying metal grain. The cell voltage did not rise above 1.5 v. The formation of an equivalent thickness of high-resistance film would require 10–15 v. The existence of a film was verified by electropolishing and etching. The film on certain metal grains dissolved first, leaving the other grains in relief.

The specimen was cleaned and anodized again for 3 hr at the same current density and temperature. Upon removal, the specimen had a variegated color pattern which seemed to vary with grain structure. The colors were not distinct enough to characterize the films in terms of interference thicknesses. In diffuse light the anodizing differences were most noticeable in terms of shades of gray, while the colors were most pronounced in reflected light. As before, the light-film areas were etched to bare metal before the dark-film areas.

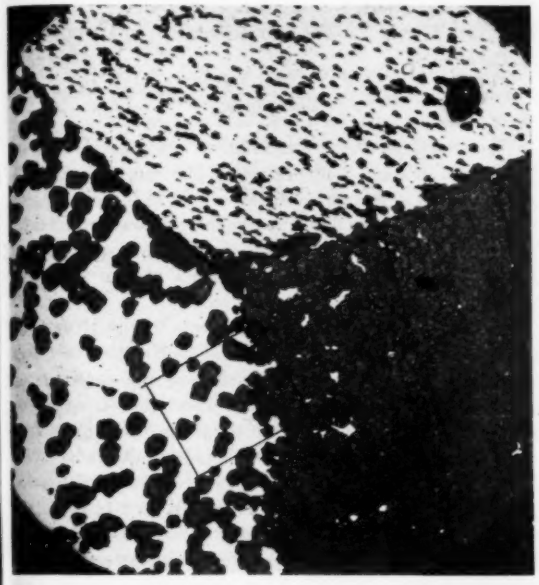

FIG. 3. Anodized pattern on hafnium crystal bar after 4 hr 10 min at 0.025 ma/cm², 70% nitric acid at 90°C. 100× before reduction for publication.

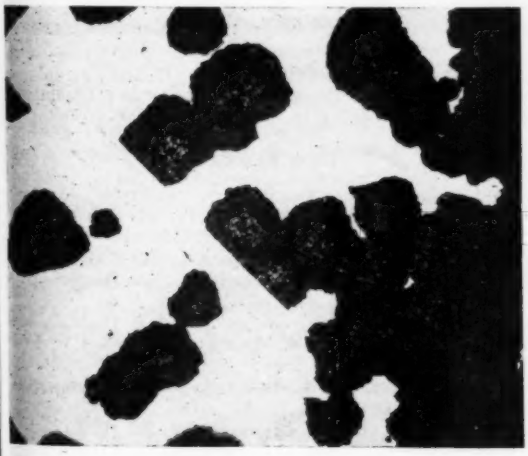

FIG. 4. Enlargement of part of the area in Fig. 3. 500× before reduction for publication.

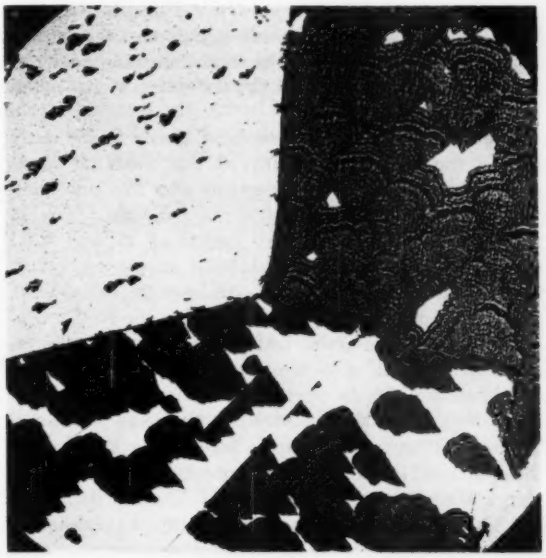

FIG. 5. Anodized pattern on hafnium crystal bar after 7 hr 30 min at 0.025 ma/cm². Pretreatment differed from that which produced Fig. 3 (same area). 100× before reduction for publication.

FIG. 6. Micrograph of the hafnium crystal bar surface after electropolishing. Same area as in Fig. 2. 500× before reduction for publication.

With the specimen in the anodized condition, the orientations of 8 metal grains were determined by the Laue back-reflection method. The grains were selected for large size and variation in shape from metallic to a bluish-black. The data are given in Table I. A more complete survey would require a quantitative measure of film thickness. The correlation between film thickness and the angular distance of the underlying crystal plane from the basal plane is similar to that observed on zirconium after the same type of treatment.

Anodizing at 0.025 ma/cm², 90°C.—The disk was anodized for 4 hr 10 min. The cell voltage rose slowly to a maximum of about 1.5 v. Selective darkening could be seen after 14 min. Upon removal, the specimen was rinsed and the surface examined.

The black oxide was concentrated chiefly in the outer area of the disk. It was observed that areas on single grains which had etched preferentially after 25°C anodizing (indicating a thinner film) were not darkened. Thus, it appeared that the initial oxide growth at 25° and 90°C may have been similar, but that the anodized areas at 90°C remained more localized. At least 20 well-defined grains were only partially darkened after the 90°C treatment. One of these grains had developed black oxide on approximately half of its area. To determine whether this difference was due to orientation differences within the grain, both areas were checked by the Laue technique. The orientation was the same. Seven other grains were then examined for surface appearance and orientation. The observations are presented in Table I. The distribution of the black oxide was not systematically dependent on orientation as in the room temperature case.

The same area as in Fig. 2 was photographed again at 100× (Fig. 3). The pattern of the oxide was distinctive. The black oxide appeared to nucleate at points and spread out over the surface. As shown in Fig. 4, the growth of black oxide stopped at a twin except at one end where the twin encountered a grain boundary. Inclusions in the surface also appeared to serve as nuclei.

The above procedure was repeated with some modification. The specimen, after repolishing mechanically and etching, was kept overnight under distilled water which was being stirred. The object was to extract any etchant which might have been trapped in crevices. The specimen was then anodized for 7 hr 30 min instead of 4 hr 10 min. The time was extended because at 4 hr 10 min only one small area on a circular face was completely black. As before, the edge of the disk darkened faster than the circular face.

The distinctive anodizing pattern is shown in Fig. 5 for the same area as presented in Fig. 2, 3, and 4. The oxide grew in the form of wedges which all pointed in the same direction within any one grain.

Effect of Electropolishing

Electropolishing was considered as a surface preparation, but was not used because of the nature of the surface that was produced. The conditions are detailed here because of an orientation effect. The disk was first wet-polished to 6 micron cloth on both faces and along the edge. It was then electropolished for eight 5-sec intervals at 100 v direct current in the acetic-perchloric electropolish. Approximately 30 sec was allowed for cooling after each polishing period. The bath was kept at about 15°C. After treatment, some grains were mirrorbright while others were slightly dull. Some of the latter exhibited faint interference colors which changed with the angle of viewing. Upon metallographic examination, the bright areas were seen to be flat while the dull areas had a furrow-like structure. The dull or matte areas exhibiting interference colors were found to have a parallel distribution of the furrows. The resultant grating would account for the interference pattern.

A micrograph of the three-grain area is shown in Fig. 6. The furrow pattern is similar to that produced on aluminum (5). The dependence on orientation is summarized in Table I.

Conclusions

The growth of oxide was influenced by orientation in two cases at room temperature: 0.025 ma/cm² and 1.5 ma/cm². In the former case, the cell voltage did not rise beyond 1.5 v and the film was evidently of lower resistance than in the latter case where the cell voltage rose to 185 v. In each case, a systematic dependence of film thickness upon metal orientation was observed.

Metal orientation also played a role in the growth of anodic oxide at 0.025 ma/cm² and 90°C, but the effect was secondary to nucleation. Comparison of the photomicrographs in this paper with those of Vermilyea (6) suggests that the oxide grew laterally in the shape of wedges. Vermilyea found that the anodic oxide on tantalum recrystallized in the form of segments which grew outward from a point. Preferred growth directions were not noted. The anisotropic growth on hafnium may have resulted from the hexagonal close-packed structure. Tantalum is body-centered cubic.

Nucleation as a factor in film growth thus appears to be associated with higher temperature. For some reason the transition to a low-resistance layer is localized. Possibly, a thicker high-resistance film may be responsible. Further work on hafnium must take account of these complexities.

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Plating Thickness by the Attenuation of Characteristic X-Rays

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ABSTRACT

When an x-ray beam of sufficient energy and intensity strikes a plated metal, it will excite a characteristic line of the substrate metal. Of the quanta excited, those properly oriented will pass through, or be absorbed by, the plating. As a consequence of the absorption, x-rays will be emitted from the plated metal at intensities less than those correspondingly obtained from the unplated. This attenuation of x-rays can be used to measure plating thickness, as has been demonstrated for tin plate and an *unresolved* x-ray beam.

In the present investigation, the attenuation by iron foil of a characteristic line from either silver or zirconium as substrate has been measured in a spectrograph provided with a good collimator and with an analyzing crystal. The results, when corrected for background, show that the exponential absorption law is followed closely. Furthermore, these results are in accord with the known mass absorption coefficients of iron, which increases confidence in the method.

Comparison of this with other x-ray methods of determining film thickness indicates that its inherent advantages are great enough to warrant its extended application.

INTRODUCTION

During the last decade, the use of x-rays to measure the thickness of thin films on thick substrates has made rapid progress.

Shortly after Clark, Pish, and Weeg (1) had obtained diffraction patterns from coatings as thin as $5(10^{-6})$ cm, three successful laboratory methods were developed for estimating thickness by use of diffraction techniques. Birks and Friedman (2, 3) used a Geiger counter to measure attenuation by a coating of a suitable x-ray line diffracted by the substrate. Gray (4) and Eisenstein (5) independently developed a photographic method in which thickness was determined by comparing the integrated intensity of a line diffracted by the coating with that of another line diffracted by the substrate.

The application of x-ray emission (x-ray fluorescence) to this important problem was begun before 1950, the year in which Beeghly (6) published results obtained in this way on tin plate. He showed that the thickness of the tin coating could be determined practically and satisfactorily by using a Geiger counter to measure the radiant energy from a sample in which the characteristic K lines of iron had been excited by a filtered polychromatic beam. In this method (Method I), the beam emerging from the substrate (iron) is attenuated by the coating (tin) and then proceeds directly to the detector through a slit. Two years later, Pellissier and Wicker (7) revealed that a similar method had been under investigation in the United States Steel Company since 1946. Also in 1952, Koh and Caugherty (8) showed that the thickness of very thin coatings could be estimated by measuring the intensity of a characteristic line of the coating (Method II). The authors used a spectrograph provided with a good collimator and with a reflecting crystal (lithium fluoride) as analyzer to measure the attenuation of a characteristic line from the substrate as a means of determining film thickness (Method III).

EXPERIMENTAL

Method III was tested on silver and on zirconium as substrate metal covered with a "plating" built up of iron foil 0.6 mil (0.00152 cm) thick. The substrate metals were chosen because their K_α lines, although differing considerably in wave length, can yet excite the K lines of iron. The use of foil made it easy to obtain "plating" thicknesses of high precision.

Under the conditions of Table I, the times for 2^{14} counts were measured for each substrate bare and covered with different thicknesses of iron foil. One background count was determined for iron near the wave length of each substrate K_α line, and the corrected counting rate for each experiment was obtained by subtracting the background counting rate from the observed. The growing importance of the background at increasing thicknesses of iron foil is clear from Fig. 1, where average counting rates, observed and corrected, are plotted as logarithmic ordinates against "plating" thickness.

DISCUSSION

In Fig. 1, virtually all the corrected average counting rates lie close to a straight line for each substrate, which means that the exponential absorption law is obeyed in each case over almost the entire thickness range. With zirconium, where the corrected counting rate varies through five powers of ten, the concordance of the results is especially impressive even though it is fortuitous at the two greatest thicknesses.

Statistical considerations show why the concordance of these last two points is fortuitous. Owing to random

TABLE I. *Experimental data for iron on silver or zirconium*
Tungsten target 50 kv and 50 ma

Thickness of iron (mils)	Silver (K_α)			Zirconium (K_α)		
	Time to 2^{14} counts (sec)	$\overline{CPS}$ (observed) (counts/sec)	$\overline{CPS}$ (corrected) (counts/sec)	Time to 2^{14} counts (sec)	$\overline{CPS}$ (observed) (counts/sec)	$\overline{CPS}$ (corrected) (counts/sec)
0	2.12	7730	7660	0.533*	30740	30700
0.6	3.00	5460	5395	1.98*	8270	8230
1.2	4.55	3600	3535	9.72	1686	1645
1.8	7.95	2060	1995	25.28	648.1	607
2.4	12.50	1310	1245	77.88	210.4	169
3.0	19.88	824	758	188.12	87.1	45.9
3.6	29.80	550	484	302.90	54.1	12.9
4.2	41.12	398	332	360.95	45.4	4.2
4.8	62.30	263	197	390.05	42.0	0.84
5.4	85.50	192	125	394.85	41.5	0.33
6.0	104.70	156	90	395.28	41.4	0.28
Background†	247.00	66	—	398.00	41.2	—

* Measured at 5 ma and listed for 50.

† Measured for iron near the wave length of the proper characteristic line.

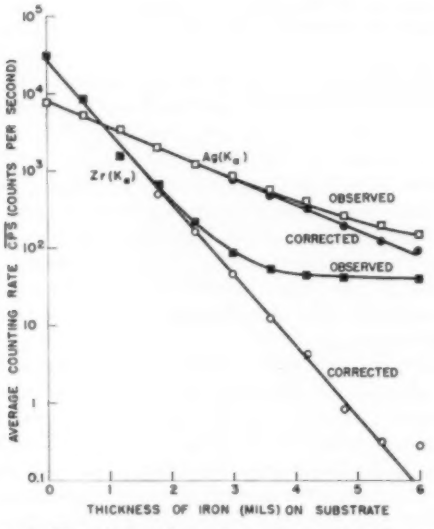

FIG. 1. Experimental results, observed and corrected for background, to test Method III in the case of iron on silver or zirconium.

fluctuations, the minimum uncertainty as measured by the "predictable standard deviation" (10) is

$$s_C = \sqrt{N_T + N_B} \qquad (I)$$

where N_T is the total and N_B the background count at the wave length of the characteristic line involved; N_B is computed for the counting interval of N_T. For Table I,

$s_C \sim \sqrt{2^{14}}$, or 2^7, at low thickness (background negligible) (II)

$s_C \sim \sqrt{2^{15}}$, or $\sqrt{2}$ (2^7), at high thickness (N_T and N_B comparable) (III)

It is easy to tell from Table I when s_C is significant relative to the number of counts used in establishing thickness. For example, at 6 mils of iron on zirconium, this number of counts is 0.28 counts/sec for 395 sec, or approximately 110 counts; and s_C is approximately 180 counts. It would not be surprising, therefore, if the corresponding point in Fig. 1 were even further from the line.

Inasmuch as the thickness measurement depends on the absorption of x-rays by iron, the results of Fig. 1 ought to be in accord with the known mass absorption coefficients of that element. Whether such accord exists can be determined by using the exponential absorption law in the form

$$\ln [I_0/I] = [\mu_1/\sin\theta_1 + \mu_2/\sin\theta_2]\rho d \qquad (IV)$$

In equation (IV), I_0/I, usually an intensity ratio, is the quotient of the corrected average counting rate for the exposed substrate by that for the substrate covered with d cm of iron foil. The mass absorption coefficients of iron are μ_1, a mean value for the incident (polychromatic) beam; and μ_2, for the characteristic line being counted. The angles θ_1 and θ_2 are those made with the sample by the incident beam (30°) and by the emergent beam (60°), the beams being regarded as rays and the surface as plane.

For present purposes, it is convenient to replace μ_1 and μ_2 by μ_{AVG}, an over-all average for incident and emergent beams. From equation (IV),

$$\mu_{AVG} = 2.303(S)/3.155\ (7.86)\ (0.00254) = 36.56(S) \qquad (V)$$

where

$$S = \log [I_0/I]/d \text{ (in mils)} = \text{Slope in Fig. 1} \qquad (VI)$$

and the numbers taken in order [1] convert the logarithms, [2] take path length (θ_1 and θ_2) into account, [3] introduce the density of iron, [4] convert from mils to centimeters.

The concordance of the results in Fig. 1 with the known mass absorption coefficients of iron may be judged from Table II.

The wave length at the K edge is the longest that can excite the coresponding K_α line, and it will therefore be somewhat greater than λ_1, the effective wave length of the incident beam. The wave length of the emergent beam λ_2 is that of the K_α line. The over-all average mass absorption coefficient should correspond to a wave length somewhere between λ_1 and λ_2. Comparison of μ_{AVG} with the known values shows that this is true, especially when allowance is made for the way in which absorption coefficients are known to decrease with wave length (9). Therefore, the conclusion is that the experimental results of Fig. 1 could have been satisfactorily predicted from known data.

Equations (V) and (VI) show that the thickness range over which the present method can be relied upon is determined largely by the value of μ_{AVG}; the larger this coefficient, the smaller this thickness range. It was found in

TABLE II*. *Test of experimental data in Fig. 1*

Substrate	S [eq. (III)]	μ_{AVG}	K_α (substrate)	K edge (substrate)	Known μ(iron)
Zr	0.944	34.7	0.78Å	0.69Å	38.5 at 0.71Å
Ag	0.333	12.2	0.56Å	0.48Å	14.0 at 0.50Å

* Known data in last three columns from Compton and Allison (9).

this connection that a single layer of 0.6-mil iron foil on a nickel substrate absorbed the K_α line of nickel so effectively that the present method was useless at this thickness. The mass absorption coefficient involved was near 400, whence S in equation (VI) exceeds 10. As is clear in Fig. 1, these considerations also help fix the thickness range over which the correction for background may be ignored. This range is near 2 mils of iron for zirconium as substrate, and about twice as great for silver.

In comparing published results for Method I (6, 7) with those given herein, it is important to remember that Method I was developed primarily for industrial control, and that equipment now available for x-ray emission spectrography was not on the market when this development began. The most important difference between the two methods is this. In Method III, improved collimation and the use of an analyzing crystal effectively eliminate interference by the characteristic lines of the coating (and by diffracted lines whatever their source). Consequently the potential difference across the x-ray tube does not have to be kept below that capable of exciting characteristic lines in the coating, as it does in Method I.

This restriction was not serious in the work on tin plate. The excitation potential of tin K_α is about 29 kv, far above that of copper K_α (about 8 kv), the line used for excitation (6). The L lines of tin, although emitted by the coating (excitation potential, 4 kv), did not interfere because they were sufficiently attenuated by air so as not to affect the detector significantly. Circumstances are quite different in the present investigation. Owing to the fact that iron K_α has a much lower excitation potential than the corresponding line of either silver or zirconium, it is not possible here to excite the substrate K_α without exciting iron K_α as well. Following are estimated K_α counting rates (counts per second) for the massive metals under the experimental conditions employed: Fe, 200,000; Zr, 32,000; Ag, 8100. Clearly Method I would fail here if K_α lines were used.

The increased potential difference available (50 kv for Table I) in Method III tends to compensate the loss of intensity that is the price of high resolution. For laboratory purposes at least, the advantages of Method III would seem to justify the additional equipment required relative to Method I.

Method III has advantages over the diffraction methods (2–5). Because the latter depend upon crystal structure, crystal orientation, and crystal size, they would seem to be more subject to uncontrolled factors than is Method III. Also, the intensity of the diffracted rays at the counter will often be less than that of the emitted.

Finally, Method III seems to complement Method II, which is restricted to very thin coatings (8, 11).

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Contribution to the Problem of Nonstoichiometry in Oxygen-Dominated Phosphors

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ABSTRACT

Oxygen-dominated phosphors of highest efficiencies are generally obtained with nonstoichiometrical compositions. This has been explained with the hypothesis that crystal defects are essential to obtain luminescence. In this paper it is postulated that the ideal, and therefore stoichiometric crystal should have maximum efficiency. The fact that an excess of one of the ingredients in general results in higher efficiency is explained with certain factors arising from the mechanism of the solid-state reactions, such as the difficulty of reaching equilibrium conditions.

The incorporation of the activator, the presence of u.v. absorbing separate phases, the problem of homogeneity of the phosphors, and the reactivity of the ingredients used for the synthesis are discussed, mainly on the basis of experimental evidence gathered in the study of the phosphors used in fluorescent lamps.

Introduction

One of the most important characteristics of phosphors used in fluorescent lamps and electronic devices is their efficiency. A great deal of work has been done, mainly in industrial laboratories, in an effort to produce phosphors of highest possible efficiency, but little has been published on the general principles involved in their synthesis.

From the beginning, phosphor chemists have recognized that very high chemical purity of the raw materials is a matter of primary importance in the preparation of highly efficient phosphors. This purity requirement is especially important with sulfide phosphors where the activator concentration is very low, such that heavy metal contamination must not exceed 10^{-5}%. With this type of phosphor, the purity of the ingredients is undoubtedly the most critical requirement in their preparation. In many cases it alone will determine the efficiency of the phosphor.

In many other phosphors, however, the activator concentration is far greater than in the sulfides, and, in consequence, the tolerance for heavy metal impurities will likewise be greater. In common phosphors such as the halophosphates and silicates, the activator concentration is of the order of 1% and the impurity limit will be of the order of 10^{-3}%. This purity is relatively easy to realize and offers no major problem to the phosphor chemist.

With these phosphors other problems arise. Even with chemicals having a purity far beyond that actually required, it may prove very difficult to prepare a silicate or a halophosphate of high efficiency. Various lots of raw materials may behave quite differently in phosphor preparation, even if the chemical analysis reveals no significant differences.

Another problem unknown in sulfide chemistry is that of the relative proportion of the basic and acidic components forming the luminescent compound. The composition of the sulfides is always practically stoichiometric, and the introduction of an excess of zinc or sulfur, for example, must be compensated for in one way or another. In oxide systems the situation is entirely different. Many patents have been granted for the attainment of unusually high efficiencies with special phosphor compositions, and various authors have correlated maximum efficiency at nonstoichiometrical compositions with the fundamentals of luminescence.

Strange (1) suggests that luminescence should not arise in perfect crystal forms, but should be associated with imperfections and dislocations. Indeed, the present theory of the luminescent centers in sulfide phosphors relates the emission to electronic transitions in lattice ions, near lattice vacancies or near foreign ions having a different valency. It does not seem probable, however, that the same applies to oxygen-dominated phosphors. The luminescence of the activated oxidic systems is of the characteristic type: the electronic transitions involved in luminescence are supposed to occur in the activating ions. It may be argued that even in this case the presence of neighboring lattice vacancies or dislocations is essential for luminescence, but then a specific influence of the activator might be expected, and the effect can hardly be considered to offer a general explanation of the principle of nonstoichiometry.

In this paper an opposite line of thought is followed. It is assumed that luminescence in oxygen-dominated phosphors, in principle, shows its maximum efficiency in perfect stoichiometrical crystals, and that various effects may tend to blur the picture, effects that are due to the history and details of the phosphor synthesis. Oxidic phosphors are generally prepared by a solid-state reaction from the oxides, or materials yielding the oxides during the firing process. The fact that these reactions seldom lead to equilibrium conditions may affect the efficiency and make it desirable to add an excess of one of the components. In this paper the following points are discussed in more detail: (*a*) incorporation of the activator; (*b*) presence of foreign materials in the fired phosphor; (*c*) fluctuations in composition from particle to particle; and (*d*) reactivity of the ingredients.

Incorporation of the Activator

One well-known phosphor system in which an excess of one of the components is required for high efficiency, is that of the halophosphates. It is reported that an excess of phosphate is necessary to obtain a good phosphor. Moreover, it is very probable that this excess of phosphate is incorporated in the crystal lattice.

Arnold (2) has shown that in precipitates of calcium phosphate an apatite structure is maintained even when the molar Ca/P ratio is 1.33 instead of the theoretical value of 1.67. The same holds for halophosphate phosphors. The authors prepared phosphors with (Ca + Mn + Sr)/phosphate ratios ranging from 1.33 to 1.75. All showed the apatite structure, and no indications of foreign substances were found, except for the presence of calcium antimonate in the materials with the highest (Ca + Mn + Sr)/P ratios. Halophosphates, therefore, might be an example of phosphors requiring an excess of one of the components within the crystal lattice for highest efficiency.

Two series of experiments were made. In the first series the composition was varied over a broad range and the efficiency of the phosphors was compared by measurements on 40-w fluorescent lamps coated with these phosphors. The phosphors were prepared by mixing $CaHPO_4$, Sb_2O_3, $MnCO_3$, CaF_2, and $SrCl_2$ in constant proportions with varying amounts of $CaCO_3$. The results are shown in Table I and Fig. 1.

In the second series of experiments the (Ca + Sr + Mn)/PO_4 ratio was varied from 1.56 to 1.67, and the efficiency of the phosphors was compared by measuring their brightness. In these samples the state of the antimony was followed by determination of its amount present in the form of trivalent antimony and the acid-insoluble rest. A similar series of samples had been prepared by Kröger (3). Trivalent antimony was determined by titration with potassium bromate and brilliant-ponceau as indicator. The acid-insoluble rest consists mainly of calcium antimonate. The results are given in Table II.

Although the antimony content was the same for all the firing mixtures it will be noted from Table II that the total antimony in the fired products is not constant. In all firings a considerable loss of antimony was found. These losses of antimony depend on the (Ca + Sr + Mn)/P ratio, and on the reactivity of the various components (*see* below).

The maximum of the efficiency curve (Fig. 1) is not very sharp. Moreover, in further experiments, its position appeared to depend entirely on the reactivity of the ingredients used and the firing conditions. This will be discussed later.

TABLE I. *Relation between the* Ca + Mn + Sr/P *ratio of halophosphates and their efficiency*

(Ca + Mn + Sr)/P ratio	Efficiency in lpw
1.33	58.0
1.42	60.6
1.50	61.1
1.56	62.0
1.65	58.3
1.75	ca. 5

However, there is a sharp drop in efficiency beyond the stoichiometric composition. This is not related to a change in the crystal lattice, since the material with a 1.75 ratio still shows the apatite structure. As Kröger pointed out the luminescence is due to trivalent antimony, and with increasing (Ca + Sr + Mn)/P ratio an increasing amount of the antimony is transformed into calcium antimonate, especially if the firing temperature is somewhat low. It is assumed that antimony substitutes for calcium. Therefore, a (Ca + Sr + Mn)/P ratio of 1.65 is the highest to allow the incorporation of sufficient antimony to obtain a good phosphor. With (Ca + Sr + Mn)/P ratios exceeding 1.67 all of the antimony in the fired phosphor is present in the form of calcium antimonate. As a consequence there is no trivalent antimony available and the substance becomes nonluminescent. This is clearly shown in Table II and Fig. 2.

The case in which an excess of the base constituent of the host crystal prevents the activator from being incorporated is not restricted to the halophosphates. The activator is a foreign constituent, and the free energy of the combination (host crystal + free activator oxide) should, in general, be smaller than the free energy of the combination (activated host crystal + free oxide of the host metal). It is a general experience that manganese-activated materials have a brownish appearance due to Mn^{3+} or Mn^{4+} provided an excess of metal is present, due to the fact that the manganese is not incorporated in the lattice. This makes it desirable to work with an excess of the acid radical in all those cases where a metallic activator is used. In this case, therefore, the nonstoichiometry has nothing to do with the necessity to create imperfections in the host crystal, but is simply a necessary requirement for the incorporation of the activator.

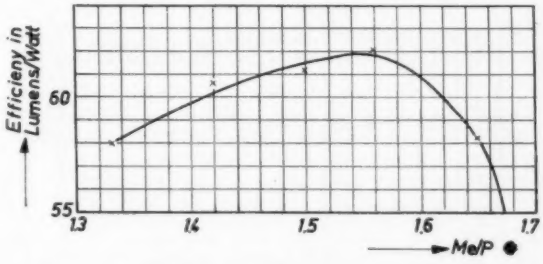

FIG. 1. Relation between the Me/P ratio of a halophosphate and its efficiency.

TABLE II. *State of the antimony and brightness of halophosphates with varying* (Ca + Mn + Sr)/P *ratios*

(Ca + Mn + Sr)/P	Weight % Sb^{3+}	Weight % insoluble residue	Rel. brightness
1.56	0.65	0.06	106
1.57	0.72	0.02	105
1.58	0.90	0.02	103
1.60	0.92	0.08	105
1.63	1.07	0.22	102
1.65	0.93	0.50	104
1.67	0.09	1.16	45

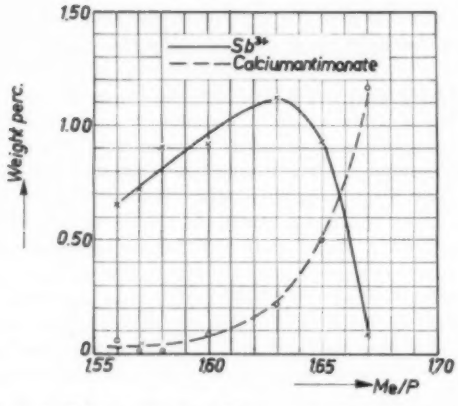

FIG. 2. Weight per cent Sb^{3+}, resp. Ca-antimonate in fired halophosphates as a function of the Me/P ratio.

TABLE III. *Effect of u.v. absorbing (antimony trioxide) and low absorbing material (unactivated halophosphate) on the brightness and luminous efficiency of a halophosphate*

% Sb_2O_3 added	Brightness of powder mixture	LPW test lamp	% Unact. haloph. added	Brightness of powder mixture	LPW test lamps
0	100	63.5	0	105	60.5
0.3	83	59.5	—	—	—
0.5	74	57.6	—	—	—
1.0	64	54.8	1	104	—
1.5	55	52.8	—	—	—
2	52	—	2	105	61.5
3	44	—	—	—	—
5	39	—	5	104	61.1
			7.5	107	59.3
			10	107	59.9
			15	101	58.8
			20	98	58.5

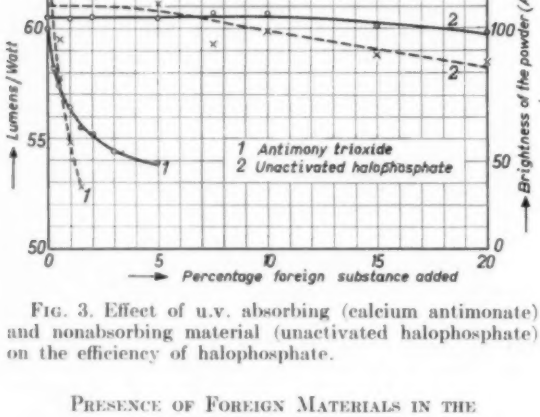

FIG. 3. Effect of u.v. absorbing (calcium antimonate) and nonabsorbing material (unactivated halophosphate) on the efficiency of halophosphate.

PRESENCE OF FOREIGN MATERIALS IN THE FIRED PHOSPHOR

As already mentioned, phosphors are generally made by means of solid-state reactions from suitable primary materials. These reactions seldom lead to entirely homogeneous products, especially in the case of phosphors, where excessive firing is preferably avoided in order to prevent the material from sintering. Therefore, it must be considered very likely that under phosphor firing conditions small amounts of the unreacted raw materials may be left in the fired phosphor. The effect of these remnants depends mainly on their ability to absorb ultraviolet radiation. If a substance is present which has a strong absorption for a certain exciting radiation, the efficiency of the phosphor will be reduced considerably, while a nonabsorbent material may have almost no deleterious effect at all.

In cathode ray excitation all foreign materials will tend to reduce the efficiency, since some or all of the energy of electrons striking the foreign materials will be lost for the purpose of excitation.

The ideas just mentioned will be demonstrated on three phosphors.

Halophosphates

To show the effect of strongly absorbing and low-absorbing foreign materials on efficiency, halophosphate phosphor was mixed with various amounts of antimony trioxide and unactivated but fired halophosphate, respectively. The u.v. absorption of the unactivated halophosphate and Sb_2O_3 is 94 and 58%, respectively.[1] The brightness data of the powder mixtures are given in Table III and Fig. 3.

To demonstrate that, under given conditions, free antimony oxide may remain as a separate phase in halophosphates the following example may be quoted. It was thought that by firing in nitrogen the formation of pentavalent antimony might be avoided and an increase of the trivalent antimony content might be obtained. An experiment was made in which varying amounts of antimony trioxide were added to the firing mixture and the firing was performed in a covered crucible placed in a stream of nitrogen. One of the fired samples showed a trivalent antimony content of 2.4%, and a brightness of 70% compared with the laboratory standard. After washing with 5*N* NaOH solution and water to dissolve the antimony trioxide not incorporated in the halophosphate lattice, the antimony content was reduced to 1.3%, while the brightness increased to 100% of the standard. This shows how strongly the presence of as little as 1% of an absorbing material may affect the efficiency of a phosphor.

Magnesium Tungstate

If a solid AB is formed by solid phase reaction from A and B, the reaction will, in general, proceed by the formation of a thin film of AB at the grain boundaries, followed by diffusion of either A or B through this layer AB. Several examples may be cited in which the u.v. absorbing component diffuses into the nonabsorbing material, and in all these cases an excess of the absorbing substance has proved to be extremely harmful to the efficiency of the phosphor. In these cases, a large excess of the nonabsorbent component is generally employed, thereby reducing the thickness of the compound layer formed and speeding up the removal of the last traces of the absorbing constituent.

[1] These figures are based on a reflectance of 77% for magnesium oxide.

An example of a reaction of this kind is the formation of magnesium tungstate from magnesium oxide and tungstic oxide. According to Jander (4), in the reaction between zinc oxide and magnesium tungstate, tungstic oxide is the diffusing agent. Therefore, one may expect that in the reaction between magnesium oxide and tungstic oxide the latter will also be the diffusing agent. This was confirmed by recent experiments by Kressin (5) in which pellets of magnesium oxide and tungstic oxide were placed on top of each other and then fired. Luminescent magnesium tungstate was formed on the surface of the magnesium oxide. The reaction between MgO and WO_3 starts with the formation of a thin layer of magnesium tungstate on the surface of the MgO and proceeds with the diffusion of WO_3 through this layer.

In the last stages of the reaction the product may be visualized as consisting of magnesium tungstate particles, with an excess of magnesium oxide in the core (either in solid solution or as a separate phase), and residues of unreacted tungstic oxide at the surface. As tungstic oxide strongly absorbs 2537 Å radiation, it will greatly reduce the luminescence efficiency of the magnesium tungstate. It has been proposed to add 100% MgO in excess of the stoichiometric composition $MgWO_4$. As a consequence, the magnesium tungstate is often referred to as Mg_2WO_5 (6). With sufficiently reactive ingredients, however, it is possible to prepare magnesium tungstate of nearly stoichiometric composition and with an efficiency comparable with that of products fired with a large excess of MgO.

This may be illustrated by the following series of values obtained on phosphors that had been prepared by making a wet paste of magnesium oxide and ammonium paratungstate, drying, and firing at 1050°C (Table IV).

Calcium tungstate.—An interesting case is furnished by calcium tungstate, where an excess of any of the components leads to the formation of ultraviolet-absorbing separate phases. As already mentioned, tungstic acid strongly absorbs 2537 Å, whereas an excess of calcium yields nonluminescent Ca_3WO_6, which also absorbs 2537 Å strongly and, therefore, also causes a drop in efficiency. In this case the only possibility of making a good phosphor is to maintain the stoichiometric formula. It is true that the addition of sulfuric acid (7) allows the use of an excess of calcium, but the function of the sulfuric acid is to neutralize any free calcium oxide that might react to form Ca_3WO_6 (8). Thus the ultimate purpose of the sulfuric acid is to maintain the stoichiometric composition of the luminescent phase itself.

Fluctuations in Composition from Particle to Particle

The idea that the core of a phosphor is different from the surface is a very common one among phosphor chemists. As a recent example Butler and co-workers (9) gave evidence that the surface of halophosphate particles must be considered to be of a different composition than the core. The question arises whether these fluctuations in composition should also extend to the different particles of a phosphor. Cohn (10) has pointed out that in a solid-phase reaction only adjacent particles may react with each other. Even in a perfect mixture only a statistical distribution may be obtained, and a situation in which every nondiffusing particle is in contact with exactly the number of diffusing particles required for obtaining the average composition will never occur in practice. This must imply that fluctuations in the composition of the individual particles of the phosphor are to be expected, and this may affect the efficiency. If, in a halophosphate, the over-all composition is exactly stoichiometric, then some of the particles might contain an excess of phosphate, while in others calcium would be in excess This excess of calcium will expel the trivalent antimony and, as already pointed out, render the particles nonluminescent.

However, it is very likely that there exists a certain interchange of ions between the particles, and this will tend to neutralize these fluctuations. The following experiments were designed to test this effect.

A normal halophosphate having a (Ca + Sr + Mn)/P ratio of 1.56 was mixed in a 1:1 ratio with an unactivated but fired halophosphate (no Sb, no Mn) having a (Ca + Sr)/P ratio of 1.68. This mixture was fired at different temperatures for 3 hr. Properties of the fired products are given in Table V.

Further details are found in a recent publication (11).

As might be expected from similar results already presented in Table III, the brightness of the unfired mixture (73%) is considerably higher than the 50% value expected from the brightness of the components (100% and 0%, respectively) and the mixing ratio alone.

The u.v. absorption has been calculated on the basis of a value of 100 for the activated material (with 0.82% Sb^{3+}). The real absorption is about 90%.

From column 3, Table V, it may be seen that the u.v. absorption increases as the firing temperature is raised. This cannot be due to the formation of calcium antimonate as practically no antimonate was analytically found in the products with the highest u.v. absorption.

The relation between the u.v. absorption and the Sb^{3+} content of halophosphates (free of calcium antimonate)

TABLE IV. *Brightness of magnesium tungstates with varying* MgO/WO_3 *ratios*

MgO/WO_3 ratio	Brightness in % of standard
0.95	61
0.98	90
1.00	93
1.01	94
1.04	90
1.10	95
1.48	99
1.98	97

TABLE V

Firing temp, °C	Brightness	U. V. abs.	$\frac{\text{Red}}{\text{Blue}}$ ratio	% Sb^{3+}	% Insoluble residue
Unfired mixture	73	75	108	0.40	Absent
1000	70	83	50	0.34	Ca. 0.1
1050	70	89	47	0.35	Ca. 0.1
1100	72	95	48	0.42	Trace
1160	67	98	43	0.40	Trace

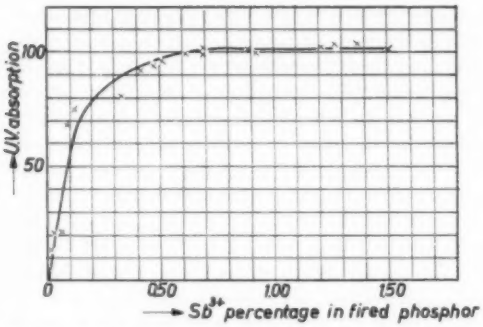

FIG. 4. Relation between the u.v. absorption of halophosphate and the Sb^{3+} content.

is given in Fig. 4. It is apparent that the u.v. absorption remains constant from about 0.60% Sb^{3+} on. Therefore, a considerable decrease of the antimony content of the above-mentioned halophosphate with 0.82% Sb^{3+} does not result in a perceptible decrease of its u.v. absorption. When Sb^{3+} is transported by a diffusion process to the unactivated halophosphate, the u.v. absorption of the latter increases. The consequence will be an increase in the u.v. absorption of the fired mixture as compared with the unfired mixture. The increase in the u.v. absorption actually found, therefore, leads to the conclusion that the Sb^{3+} ions are mobile at the firing temperatures employed.

It can be concluded further from these experiments that the Ca^{2+} ions are also mobile. The unactivated halophosphate has the high (Ca + Sr)/P ratio of 1.68. We have seen that such a halophosphate can contain only a very small amount of Sb^{3+}. Firing a halophosphate with this composition in air results in a nearly complete transformation of Sb_2O_3 into the calcium antimonate. From the u.v. absorption it follows that the unactivated halophosphate has taken up Sb^{3+}. This can only be possible if the (Ca + Sr)/P ratio has decreased by transfer of Ca^{2+} ions (and Sr ions) from the unactivated to the activated halophosphate.

The simultaneous distribution of the Mn^{2+} ion between the particles of the two samples of halophosphates can be inferred from the decrease of the red/blue ratio, because the intensity of the Mn-band (peak wave length of 5800 Å) decreases in a halophosphate at decreasing Mn^{2+} content. At a higher firing temperature the red/blue ratio decreases as compared with a lower firing temperature. This is due to the increase of the mobility of the Mn^{2+} ions at higher temperatures.

The possibility that the fired mixture might consist of an Sb-activated and, therefore, blue luminescent phosphor as a separate phase next to the original Sb-Mn-activated phosphor, was ruled out by microscopic examination which showed that a homogeneously colored material was obtained.

Summarizing, it is concluded that from a temperature of about 1000°C on Ca^{2+}, Mn^{2+}, and Sb^{3+} ions in halophosphates are interchangeable between halophosphate particles of different compositions. Thus, local deviations from the average composition, caused by incomplete mixing, will tend to be equalized in the firing process by transport of Ca^{2+} ions from particles with higher, to particles with lower (Ca + Sr + Mn)/P ratio. However, a small excess of phosphate should help considerably to avoid a local excess of calcium, and this might be another reason for its practical use.

Reactivity of the Ingredients

As mentioned in the introduction, the study of the chemistry of phosphor preparation has been concentrated largely on the purity of the ingredients, whereas considerations regarding their reactivity, which depends on properties such as particle size and surface activity, have been restricted to the desirability of maximum reactivity. Sufficiently high reactivity is, of course, very important. In order to obtain a good phosphor, it may prove advantageous, however, to employ one or more ingredients deliberately in a less reactive condition. This may be illustrated by means of two examples.

To prepare zinc beryllium silicate, zinc oxide, silica, beryllium oxide, and manganous carbonate are usually mixed and fired at 1150° – 1250°C. As Froelich has pointed out (12), it is most important that the zinc oxide should be sufficiently reactive toward the silica, otherwise the growth of zinc oxide particles interferes with this reaction. The authors found that beryllium oxide behaves quite differently. It proved very difficult to incorporate the manganese if the beryllium oxide was too reactive; the phosphors had a brownish tinge after firing and the efficiency remained low. Prefiring this reactive beryllium oxide in order to make it less reactive caused a definite improvement. The method of mixing also had an effect. Ball milling the dry ingredients yielded a better phosphor than ball milling in alcohol, followed by drying (13).

Beryllium oxide that is too coarse will also produce inferior phosphors. It must be concluded that a well balanced combination of reactivities is required in order to obtain maximum efficiency of the phosphor.

Another example of the fact that a too highly reactive component may cause trouble was encountered in the preparation of halophosphates from calcium hydrogen phosphate, calcium carbonate, calcium fluoride, strontium chloride, antimony oxide, and manganous carbonate. Here the use of a very reactive calcium fluoride resulted in a shift of the emission color toward the green and a very rapid deterioration of the quartz vessels in which the firing was carried out (14). With coarser calcium fluoride, the other ingredients and the firing conditions remaining the same, it was found that some calcium fluoride may be left unreacted (11). This may explain the shift of the color toward green, when a more reactive CaF_2 is used. Another possibility is that an early incorporation of the fluorine during the firing process makes it more difficult for the chlorine to enter the lattice.

The simplest way of correcting for a lack of reactivity of a component is to increase its relative amount in the firing mixture. Froelich has already pointed out (12) that, in the batch composition of a phosphor, the surface area of the ingredients should be considered rather than the absolute quantities. The question whether this really holds will depend on the firing process. If a phosphor is underfired, then indeed the surface area of the raw ma-

terials must be the factor determining the completeness of the reaction, whereas firing at a higher temperature or increasing the firing time will tend to reduce the influence of the surface area and the relative quantities will be more important instead.

As an example to show how the reactivity of one of the components may influence the chemical properties of the fired phosphor reference may again be made to the halophosphates. As the calcium hydrogen phosphate used for its synthesis gets coarser, the reaction between the excess phosphate and the calcium antimonate formed during the firing becomes increasingly more difficult. As a consequence, more of the antimony will be found in the form of antimonate, and less antimony will be incorporated in the trivalent state. Increasing the firing time and/or the firing temperature will favor the reaction and result in an increased Sb^{3+} content. On the other hand, the volatilization of the antimony as the chloride is found to be stronger with a more reactive calcium hydrogen phosphate, or with a larger excess of phosphate. The latter effect is demonstrated in Table II. A more detailed account of the other effects will be given in a paper to be published in the future.

The examples given here will suffice to show that there is a close connection between the reactivity of the ingredients and their relative amounts as used in the synthesis of a phosphor. The reactivities of the components will therefore be reflected in the formula finally adopted for the large-scale production of a phosphor. This formula may also be expected to offer some protection against inevitable variations in reactivity of the ingredients from batch to batch and, therefore, in general, will deviate more or less from the stoichiometric composition.

Conclusion

Summarizing, it may be stated that, for the phosphors discussed in this paper, there is no reason to postulate that an excess of one of the components is an essential point in order to obtain a luminescent material with a high efficiency. An excess of one of the components often helps to facilitate the incorporation of the activator, or to avoid the presence of u.v. absorbing materials in the fired phosphor. Therefore, in practice, using an excess of one constituent will generally be preferred over a procedure relying on exact stoichiometric formulation. No indications have been found in the authors' work on phosphors which are commonly employed in fluorescent lamps that nonstoichiometry has a fundamental meaning in these phosphors.

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1956 Journal.

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Studies on the Mechanism of the Electrolytic Formation of Perchlorate

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ABSTRACT

Current-potential curves of the electrolytic oxidation of chlorate were determined polarographically using a platinum microanode. The nature of the polarogram thus obtained was quite different from that of the usual oxidation-reduction process. Two potential stages were found; the lower one is believed to be the potential of oxygen evolution and the higher one the potential of perchlorate formation. Probably the limiting current for the oxidation of water could also be seen in the polarogram.

Electrolysis of chlorate solution at definite anodic potentials corresponding to the higher stage of the polarogram was carried out in order to confirm the results of the polarographic study. From these experiments, it was clear that the first step of perchlorate formation was probably the discharge of chlorate ion at higher potential than that of oxygen evolution.

INTRODUCTION

Production of perchlorate is the typical electroprocess which cannot be carried out successfully by any other method.

The anodic potential of the formation of perchlorate has been considered to be very high, and this electrolytic preparation has been successfully accomplished only by use of a smooth platinum anode which has the highest oxygen overvoltage. A new electrolytic process for this product was developed, using a lead peroxide anode instead of platinum (1). In this case, a small amount of sodium fluoride must be added to the electrolyte to increase the oxygen overvoltage on the lead peroxide anode. The reason for this device is that the potential for anodic formation of perchlorate is very high, but it may still occur at a potential lower than that of oxygen evolution. However, it has not yet been accurately determined, and its variation with chlorate concentration is also unknown. Therefore, the present study seeks to measure accurately the anodic potential of perchlorate formation and, at the same time, to present the most probable mechanism of this process.

ANODIC POLAROGRAM OF THE ELECTROLYSIS OF CHLORATE BY A PLATINUM MICROANODE

The electrolytic reduction potentials of organic compounds, which are lower than those of hydrogen evolution at the dropping mercury cathode, and the variation of these potentials with concentration of the depolarizer can be measured polarographically. The same principle was applied to the anodic process of perchlorate formation. If the anodic potential of perchlorate formation is lower than that of oxygen evolution at a platinum anode, a typical anodic polarogram will be obtained by a platinum microanode. A hypothetical polarogram is shown in Fig. 1.

Variation of anodic potential with chlorate concentration is represented approximately by the following formula:

$$E = \frac{RT}{2F} \ln \frac{K}{C_{ClO_3^-} a^2_{OH^-}} \qquad (I)$$

where $C_{ClO_3^-}$ is the concentration of chlorate, K is a constant, and the other symbols have their usual significance. If these assumptions are verified by experiments, the formation of perchlorate must be expressed by the following mechanism (2):

$$2\,OH^- - 2e \rightarrow 2\,OH \rightarrow O + H_2O \qquad (II)$$

$$ClO_3^- + O \rightarrow ClO_4^- \qquad (III)$$

On this basis, current-potential curves of the electrolytic oxidation of chlorate were determined polarographically under various conditions.

Measurement of Current-potential Curves

A micro rotating platinum electrode and a smooth platinum plate of large area were used as anode and cathode, respectively. Details of cell design and measuring circuit are shown in Fig. 2*a* and 2*b*.

Electrolytic cell.—A section of 0.3 mm diameter platinum wire sealed in a glass tube was used as the anode and gave an area of 10^{-3}–10^{-4} cm². The cathode was a 10 mm² platinum plate. Throughout the electrolysis, the current was less than 7×10^{-4} amp. The stem of the anode—a glass tube—was rotated at 1000 rpm, which prevented accumulation of oxygen gas on the anode surface and maintained constant thickness of the anodic diffusion layer during the measurement. Better reproducibility in the measured current-potential curves may therefore be expected.

Polarograph.—Sensitivity of the galvanometer used was 3.5×10^{-6} amp/mm/m.

Apparatus for the cathodic potential measurement.—When the cathode has a large area and the current is very small, it is generally expected that polarization at the cathode is very small. In this case, however, it amounted to about 500 mv at 3.5×10^{-3} amp/cm². Thus, the cathodic potential had to be measured continually throughout the current-potential curve determination. For this purpose, the simple apparatus illustrated in Fig. 2*b* was

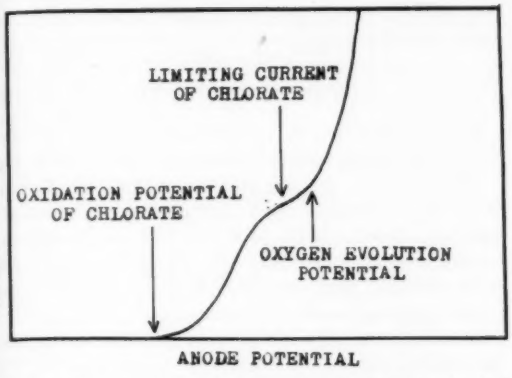

FIG. 1. An assumed polarogram in which the potential of perchlorate formation is lower than that of oxygen evolution.

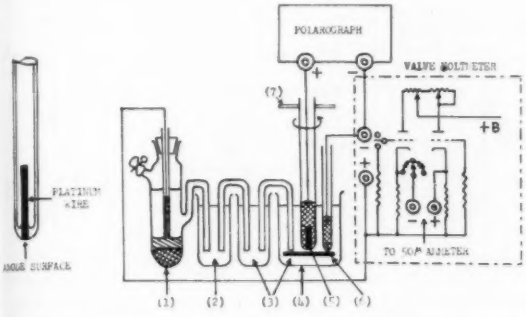

FIG. 2*a* and 2*b*. (*Left*) Details of the anode (2*a*); (*right*) the electrolytic cell, also the apparatus of the cathodic potential measurement (2*b*) for the polarographical measurement, 1—saturated calomel electrode, 2—KCl saturated solution, 3—electrolytic solution, 4—electrolytic cell, 5—anode, 6—cathode, 7—stroboscope.

satisfactory. It had a sensitivity of 3 mv and a range of −450 to +450 mv.

Temperature.—The electrolytic cell and the calomel electrode were immersed in a thermostat regulated at 17° ± 0.02°C.

Electrolyte.—Aqueous solutions of sodium chlorate (1–6M) were used. Such high concentration of the electrolyte, together with the relatively large anodic current density described above, makes the condition of the present current-potential curve measurement quite different from that of the ideal polarographic method. But well-known anodic processes of lower potential than that of oxygen evolution were carried out in the same apparatus and under the same conditions; they gave their normal polarograms.

Results and Discussion

Anodic polarograms[1] are shown in Fig. 3. The abscissa corresponds to the anodic potential on the hydrogen scale, the numerical values of which were obtained by subtracting the cathodic potential from the cell voltage. The ordinate corresponds to the apparent anodic current density in amperes per square decimeter. Its value, however, was not so reliable in view of the unknown true area of the anode.

Some characteristics of the polarograms are:

1. In a moderately concentrated solution of chlorate, two stages of potential were definitely observed.

2. In the first, or lower stage, the potential is between 1.7 and 1.9 v; in the second, or higher stage, it is higher than 2.3 v.

3. Contrary to the usual polarogram, the height of the wave of the first potential stage was seen to be inversely proportional to the concentration of chlorate.

4. For a sufficiently dilute solution, this wave height grew so high that it reached beyond the range of the measurement, a simple exponential curve being observed.

If an analogous interpretation were made for these polarograms compared to the usual cathodic ones, the first stage would be the potential of the chlorate oxidation and the second one would be for oxygen evolution. This, however, is denied by the fact that the height of the wave corresponding to the first stage is inversely proportional to the chlorate concentration. In addition, the value of the potential of the first stage corresponds to that of oxygen evolution. The reversible oxygen potential is about 0.8 v for any solution of *p*H 7. Estimating about 1 v for oxygen overvoltage on smooth platinum at 1 amp/dm², the actual oxygen evolution potential for any solution concerned amounts to about 1.8 v.

If the lower potential corresponds to the electrolysis of water and is the potential of oxygen evolution, the higher one is that of the chlorate oxidation. Thus, these polarograms should be classified as another type of the current-potential curve, different from those of the ordinary oxidation reduction process. It is certain that the oxidation of chlorate occurs at a potential higher than

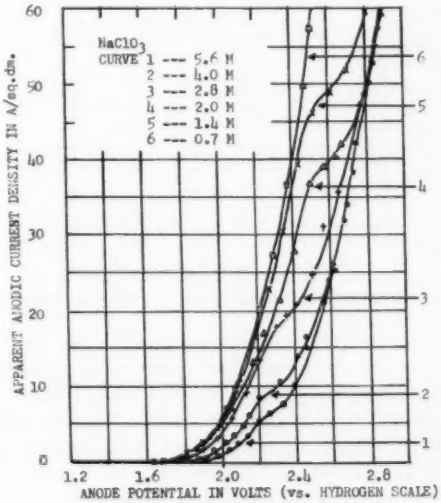
NaClO3
CURVE 1 --- 5.6 M
2 --- 4.0 M
3 --- 2.8 M
4 --- 2.0 M
5 --- 1.4 M
6 --- 0.7 M
APPARENT ANODIC CURRENT DENSITY IN A/sq.dm.
ANODE POTENTIAL IN VOLTS (vs. HYDROGEN SCALE)

FIG. 3. Anodic polarograms of $NaClO_3$. The potentials of the second stage are about: 2.3 v for 5.6M solution, 2.3 v for 4.0M solution, 2.5 v for 2.8M solution, 2.6 v for 2.0M solution, 2.7 v for 1.4M solution.

[1] The polarograms shown in this paper (Fig. 3, 4, 5, and 10) are not a common photograph, but a plotting curve of current against applied voltage.

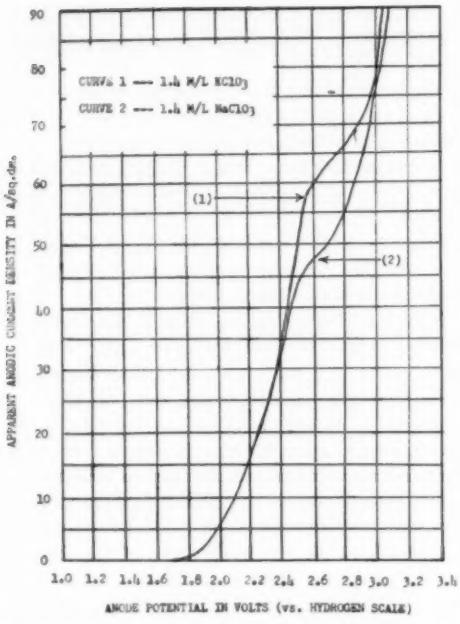
CURVE 1 — 1.4 M/L KClO3
CURVE 2 — 1.4 M/L NaClO3
(1)
(2)
APPARENT ANODIC CURRENT DENSITY IN A/sq.dm.
ANODE POTENTIAL IN VOLTS (vs. HYDROGEN SCALE)

FIG. 4. Anodic polarograms of 1.4M $NaClO_3$ and 1.4M $KClO_3$.

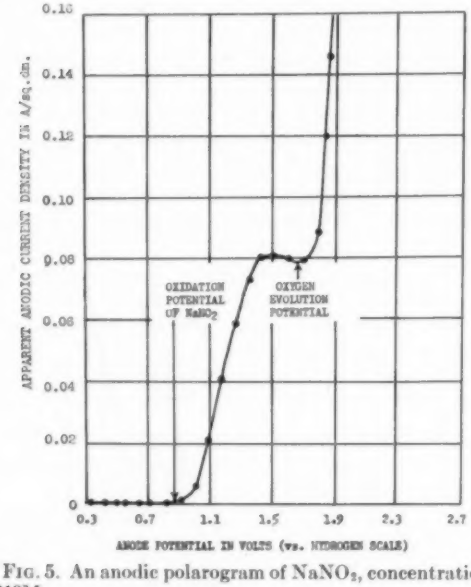
OXIDATION POTENTIAL OF NaNO2
OXYGEN EVOLUTION POTENTIAL
APPARENT ANODIC CURRENT DENSITY IN A/sq.dm.
ANODE POTENTIAL IN VOLTS (vs. HYDROGEN SCALE)

FIG. 5. An anodic polarogram of $NaNO_2$, concentration—0.013M.

that of oxygen evolution. These facts are not explainable by the mechanism of equations (II) and (III).

An alternative mechanism was adopted by the authors in which discharge of chlorate ion was assumed. This may be formulated as follows:

$$2ClO_3^- - 2e \rightarrow 2ClO_3 \text{ (or } O_3Cl \cdot ClO_3) \quad \text{(IV)}$$

$$2ClO_3 + H_2O \rightarrow HClO_3 + HClO_4 \quad \text{(V)}$$

or

$$ClO_3^- - e \rightarrow ClO_3 \quad \text{(VI)}$$

$$OH^- - e \rightarrow OH \quad \text{(VII)}$$

$$ClO_3 + OH \rightarrow HClO_4 \quad \text{(VIII)}$$

This mechanism (IV, V) has been proposed by others (3, 4), but experimental verification has been lacking.

The reason for the possibility of chlorate ion discharge at a higher potential than that of oxygen evolution is based on a decrease of the activity of water in the neighborhood of the anode surface. This can be ascribed to the extraordinarily high concentration of the electrolyte and to the hydration power of existing ions.

In order to throw some light on the latter assumption, the polarograms of 1.4M solutions of $NaClO_3$ and of $KClO_3$ were made (Fig. 4).

In Fig. 4 the wave height of the first potential stage of

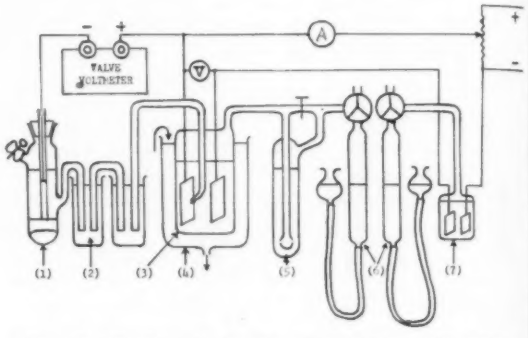

FIG. 6a. Equipment for the electrolysis of $NaClO_3$ at definite anodic potential, 1—saturated calomel electrode, 2—KCl saturated solution, 3—electrolytic cell, 4—water bath (cooling water), 5—2*N* KI solution (acidified), 6—gas buret, 7—detonating gas coulometer.

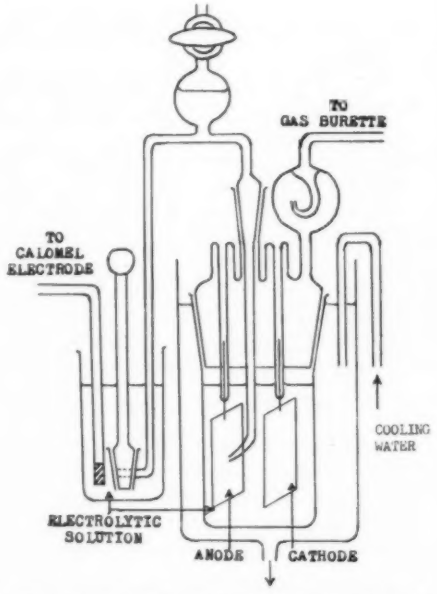

FIG. 6b. Electrolytic cell for the electrolysis of $NaClO_3$ at definite anodic potential.

$NaClO_3$ was found to be lower than that of $KClO_3$. This is taken as being related to the difference in hydration powers of Na^+ and K^+, which may be the reason for the difference in current efficiency of perchlorate formation from various chlorates (5).

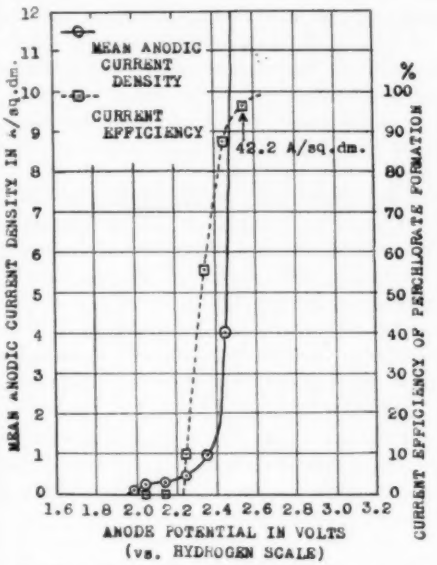

FIG. 7. Electrolysis of 5.58M $NaClO_3$ at constant anodic potential. Effect of applied anodic potential (also of anodic current density) on the current efficiency of perchlorate formation.

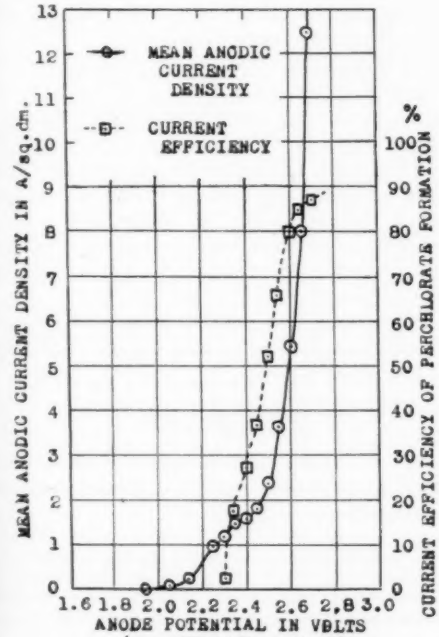
MEAN ANODIC CURRENT DENSITY
CURRENT EFFICIENCY
MEAN ANODIC CURRENT DENSITY IN A/sq.dm.
CURRENT EFFICIENCY OF PERCHLORATE FORMATION
%
ANODE POTENTIAL IN VOLTS (vs. HYDROGEN SCALE)

FIG. 8. Electrolysis of 1.36M $NaClO_3$ at constant anodic potential. Effect of applied anodic potential (also of anodic current density) on the current efficiency of perchlorate formation.

In order to confirm the accuracy of the polarographic method, current-potential curves were made for several typical anodic reactions (electrolysis of KCl, KBr, KI, $NaNO_2$, $Na_2S_2O_3$, Na_2SO_3, etc.) which seemed to occur at a lower potential than that of oxygen evolution. In the polarograms thus obtained, the potential stage corresponding to each anodic reaction was observed definitely

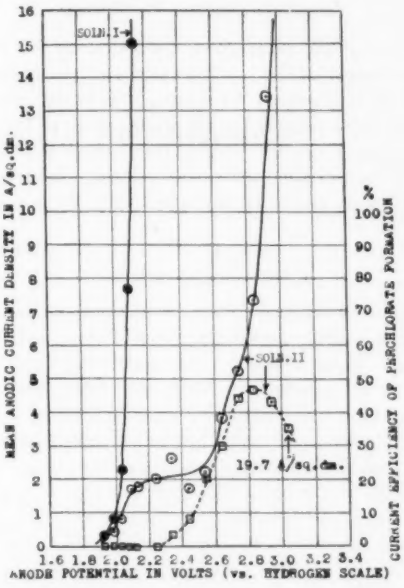

FIG. 9. Electrolysis of 0.11M $NaClO_3$ (solution I) and 0.11M $NaClO_3$ plus 1.25M $NaClO_4$ (solution II) at constant anodic potential. Effect of applied anodic potential (also of anodic current density) on the current efficiency of perchlorate formation.

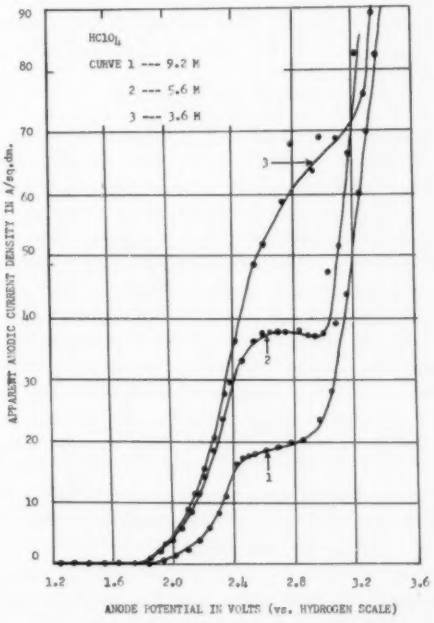

FIG. 10. Anodic polarograms of $HClO_4$

at lower potential than that of oxygen evolution (Fig. 5).

These results showed that the polarogram of the electrolytic oxidation of chlorate described above and the proposed mechanism based on the polarogram were both probably correct.

Electrolysis of Chlorate Solution at Definite Anodic Potentials

In view of the prospective discussion on the relationship between chlorate ion discharge and perchlorate formation, it is necessary to confirm the formation of perchlorate at the potential of the second stage of the polarogram in Fig. 3. For this purpose the electrolysis of chlorate solution was carried out under various conditions at a definite anodic potential corresponding to the second stage in Fig. 3.

Experimental Procedures

An aqueous solution of sodium chlorate and a mixture of it with sodium perchlorate were electrolyzed under a series of constant anodic potentials. The current efficiency of perchlorate formation was determined mainly by comparing the volume of gases generated from the electrolytic cell and from a gas coulometer in series. The circuit and gas measuring apparatus are shown in Fig. 6*a*. Details of the electrolytic cell are shown in Fig. 6*b*.

The anode and cathode were both of smooth platinum plate; the apparent areas were about 10 cm². The anode potential was measured directly by means of a valve voltmeter. Cell temperature was maintained at 17°–20°C during electrolysis.

For each electrolysis, 200 cc of the solution were employed. Each run was carried out to obtain a single point of the curves in Fig. 7–9. Throughout each electrolysis, ⅙ amp-hr of electricity was passed, and the average anodic current density was calculated by dividing the amount of current by the duration of electrolysis.

Results and Discussion

At first, 5.58 m/l and 1.36 m/l sodium chlorate solution were subjected to electrolysis under constant anodic potential, and the anodic current density and the current efficiency of perchlorate formation at that current density were plotted against the applied anodic potential. A current-potential curve was obtained from these experiments. Examples are shown in Fig. 7 and 8.

The character of the current-potential curve was similar to that of the curves obtained by the polarographic method. The current efficiency of perchlorate formation increased with increasing current density due to the increase of applied anodic potential. In the case of 5.58 m/l solution, it reached above 90% at a potential of nearly 2.55 v (C. D. 42.2 amp/dm²). Oxygen evolution began at a potential lower than that of perchlorate formation and continued to evolve together with perchlorate formation with a very poor efficiency.

Next, a similar experiment was carried out using 0.11 m/l chlorate solution and a mixed solution of 0.11 m/l chlorate and 1.25 m/l perchlorate. The current-potential curves obtained are shown in Fig. 9.

In the case of 0.11 m/l chlorate solution, the current-potential curve was quite simple and became exponential at 1.95–2.15 v. This showed that oxygen evolution was the only reaction which occurred. When the same amount of chlorate in 1.25 m/l perchlorate solution was electrolyzed, a curve having two potential stages similar to Fig. 8 was obtained. This showed clearly the occurrence of perchlorate formation with a fair current efficiency. This seems to be the reason for the almost perfect conversion of chlorate to perchlorate by the electrolysis on a commercial scale.

In this experiment, if a potential higher than 2.85 v was applied (current being increased with the applied potential), the current efficiency of perchlorate formation was again decreased, and oxygen evolved vigorously. This phenomenon may be due to the discharge of perchlorate ion. In this connection, the polarograms of perchloric acid obtained in the same apparatus are shown in Fig. 10.

In these polarograms,[2] two potential stages were observed, just as in the case of the polarograms of Fig. 3. As described above, the first stage corresponds to the potential of oxygen evolution and the second stage to the potential of the discharge of ClO_4^- ion. This gives[3]

$$ClO_4^- - e \rightarrow ClO_4 \qquad (IX)$$

$$ClO_4 \rightarrow ClO_2 + O_2, O_3, \text{etc.} \qquad (X)$$

Conclusion

1. It was proved that the first step of perchlorate formation was the discharge of chlorate ion at a higher potent than that of oxygen evolution.

2. It is suggested that the discharge of chlorate ion is possible not only because of the high oxygen overvoltage on special anodic materials, but also the decrease of the activity of water in the neighborhood of the electrode surface. The latter follows because of the extraordinarily high salt concentration of the electrolyte and because c the strong hydration power of existing ions.

3. High anodic current density is one of the necessary conditions for maintaining the anodic potential at highe values suitable to the discharge of ClO_3^- ion.

4. The complete conversion of chlorate to perchlorate is due to the co-existence of a large amount of perchlorate in the same solution.

Acknowledgment

The aid of a grant for fundamental scientific research from the Ministry of Education of Japan is gratefully acknowledged.

[2] The effect of temperature upon the wave height of the first potential stage was exactly measured for 9.2M solution of perchloric acid. The increase of the limiting current due to the increment of temperature was definitely observed. The result may be reported later.

[3] The occurrence of these reactions has already been reported by other investigators (6). The authors also confirmed it by the electrolysis.

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Any discussion of this paper will appear in a Discussion Section, to be published in the June 1956 JOURNAL.

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Fusion Electrolysis of Bismuth Trichloride

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ABSTRACT

Bismuth has been deposited from a fused electrolyte containing 33 wt % bismuth trichloride in a lithium chloride-potassium chloride eutectic mixture as carrier salt at approximately 400°C. The electrolyte was maintained at the desired temperature by the electrolyzing current, requiring 1.27 kwhr of power per pound of bismuth deposited. The cathode current efficiency was nearly 100% and the average yield was 88.8%. The process readily lends itself to continuous operation.

INTRODUCTION

Although the use of aqueous solutions for electrodeposition and electrorefining of bismuth has attracted considerable attention, very little has been reported in the literature concerning fused electrolytes. Early attempts to prepare bismuth by fusion electrolysis of bismuth trichloride were discouraged by the high solubility of the metal in the molten salt. In 1900 Helfenstein (1) reported that no metal regulus was obtained upon electrolysis of molten bismuth trichloride. The electrolyte became dark colored during electrolysis and the solidified melt was permeated with bismuth, giving the salt a metallic luster. Grossbach (2) electrolyzed bismuth trichloride at 340°C for 16 hr, using a 2-amp current, and obtained a 49.3% yield of bismuth. He pointed out that the phase diagram for the system bismuth-bismuth trichloride indicated that prolonged electrolysis was necessary before bismuth metal was obtained. Cleary and Cubicciotti (3) determined the solubility of bismuth in bismuth trichloride to be 47.5 mole % at 450°C. They investigated the effect which addition of other chlorides had on this solubility and reported that the larger the anion to cation ratio of the added salt, the less effective the salt in reducing the solubility, and the more electropositive the cation of the added salt, the more effective the salt in reducing the solubility. Recently Morris, Douglass, and Vaughn (4) reported successful deposition of bismuth from fused electrolytes containing 10 or 25% bismuth trioxide in a calcium chloride-sodium chloride eutectic mixture or in the individual salts at temperatures of 600°–900°C.

The present work was undertaken in an effort to determine if the solubility of bismuth in bismuth trichloride could be reduced sufficiently by the presence of other salts to permit a feasible electrolysis to be carried out. A lithium chloride–potassium chloride eutectic mixture was chosen as the carrier salt because it has a low melting point (352°C) and because it meets the recommended qualifications (3) for reducing effectively the solubility of bismuth in bismuth trichloride. Although a lithium chloride-sodium chloride mixture would have provided the most electropositive cations, the higher melting point of the eutectic (552°C) would have been a disadvantage.

Since no ores in this country are mined chiefly for their bismuth content, no work with ores was carried out; however it is of interest to note that chlorine metallurgy has been employed in the treatment of bismuth ores in Romania (5). Pulverized ore containing 37.5% bismuth was chlorinated at 500°C, and distilled bismuth chlorides were collected in glass condensers. Wet chemistry was then employed for purification and preparation of bismuth subnitrate or, alternatively, bismuth metal was recovered by cementation on iron bars.

Rogers and Campbell (6) have recently reported the preparation of high-purity bismuth trichloride by chlorination of crude bismuth metal.

EXPERIMENTAL

Apparatus and Materials

The electrolytic cell used in the experimental work is shown in Fig. 1.

Direct current was supplied by a 25 v, 50 amp selenium rectifier and alternating current by a 3 kw welding transformer. An ampere-hour meter was included in the d-c circuit.

All of the chemicals used were Baker "Analyzed Reagent" grade. The eutectic mixture was prepared in 1 kg lots by mixing 59 mole % lithium chloride with 41 mole % potassium chloride and melting the mixture under vacuum at 450°C. The solidified salts were broken up and stored in a tightly stoppered bottle.

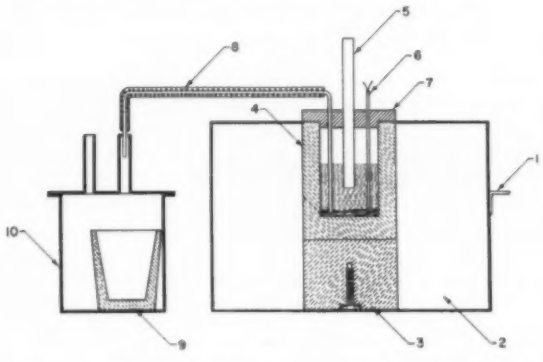

FIG. 1. Schematic diagram of electrolysis cell and auxiliary equipment. The various components are: 1, cathode connection welded to steel shell; 2, insulation; 3, graphite block bolted to steel shell; 4, graphite crucible; 5, graphite rod anode; 6, Vycor thermocouple well; 7, asbestos-cement board cover; 8, Vycor siphon tube wrapped with heating tape; 9, clay crucible; 10, steel container attached to vacuum line.

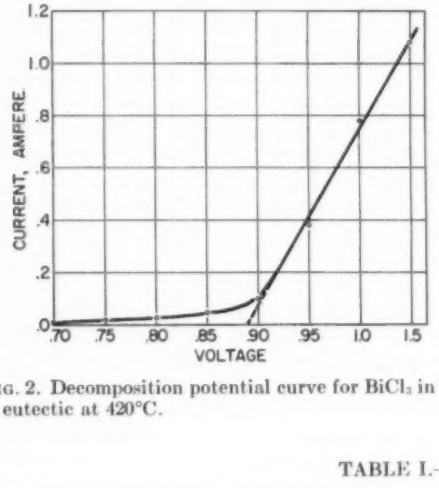

FIG. 2. Decomposition potential curve for $BiCl_3$ in LiCl-KCl eutectic at 420°C.

Procedure

At the start of each run, 200 g of eutectic salt mixture were melted in the cell with alternating current from the welding transformer, using a ¼ in. diameter graphite rod electrode. When the molten salts were at the desired temperature, the alternating current was disconnected, 100 g of bismuth trichloride were added, the cover replaced, and the direct current was connected. The current was somewhat erratic for a minute or two while the bismuth trichloride was melting, but could soon be adjusted to a constant value. In all the experiments the graphite crucible was made cathodic and the central graphite rod was made anodic. Bismuth depositing at the sidewalls of the crucible dropped to the bottom and accumulated there. Every 15 min additional bismuth trichloride was added, the amount depending on the magnitude of the current employed, assuming the depletion of bismuth trichloride from the electrolyte to be taking place at 100% current efficiency. Addition of bismuth trichloride to the cell was always accompanied by fuming, so an effort was made to minimize volatilization losses by adding the bismuth trichloride as rapidly as possible and replacing the cover immediately.

To recover the deposited metal, the heated siphon tube was placed in the crucible and the molten bismuth was siphoned over by applying a vacuum to the receiving container. Molten bismuth was removed from the cell when 65–70 ml of metal had accumulated.

The anode was raised periodically to prevent short-circuiting as bismuth accumulated at the bottom of the cell. As the surface level of the electrolyte was raised, more salts deposited on the cover from spray produced by chlorine evolution at the anode. From this standpoint, it was advantageous to keep the surface level as low as possible by periodically removing the deposited metal.

Decomposition potential

To determine the decomposition potential of the electrolyte, a cell similar to the one shown in Fig. 1, was used; nichrome heating elements maintained the temperature constant. The electrolyte contained 33% bismuth trichloride by weight in a lithium chloride-potassium chloride eutectic carrier salt mixture at 420°C. Fig. 2 shows current values plotted as a function of voltage. Extrapolation of

TABLE I.—*Data for bismuth deposition*

Experiment No.	Duration, hr	Cell voltage	Current, amp	Temp, °C	Cathode current density amp/dm²	Wt $BiCl_3$ consumed, g	Wt Bi recovered, g	Cathode current efficiency, %	Yield, %	Kwhr/lb Bi
1	6	6.4	38.5	394	26.4	949	585	97.5	93.0	1.15
2	6	7.2	46.2	426	31.6	1,230	703	97.8	86.2	1.29
3	6	6.7	44.5	409	30.5	1,135	676	97.3	89.9	1.20
4	7	7.7	34.3	402	23.5	1,080	583	93.2	81.5	1.44
5	7	6.9	39.4	406	27.0	1,210	706	98.5	88.0	1.22
6	16	6.9	38.4	403	26.3	2,480	1,452	90.9	88.3	1.33
7	7	6.9	39.7	400	27.2	1,160	708	98.0	92.1	1.23
8	6	7.6	38.8	404	26.6	980	597	98.5	92.0	1.35
9	7	6.8	44.7	385	30.6	1,340	758	93.2	85.4	1.27
10	10	6.7	39.3	392	26.9	1,580	961	94.2	91.8	1.24

the steep portion of the curve to zero current gave a value of 0.89 volt for the decomposition potential.

From the data of Villa (7) the free energy of the reaction

$$\tfrac{1}{3}Bi\ (1) + \tfrac{1}{2}\ Cl_2\ (g) = \tfrac{1}{3}\ BiCl_3\ (1)$$

is -20.1 ± 1.5 kcal at 420°C. To obtain the free energy of the reaction occurring in the electrolysis cell:

$$\tfrac{1}{3}\ Bi\ (1) + \tfrac{1}{2}\ Cl_2\ (g) = \tfrac{1}{3}\ BiCl_3\ (1, M\% = 0.081)$$

$\frac{1}{3}\ RT$ ln (0.081) must be added to the -20.1 the result being -21.2 ± 1.5 kcal or 0.92 ± 0.06 volt. This value is in good agreement with the decomposition potential determined experimentally, indicating that the cell reaction was essentially that postulated.

Discussion of Results

Data pertaining to the electrolysis tests are shown in Table I. In all cases the molten electrolyte remained clear enough that bismuth metal was visible at the bottom of the cell.

Calculation of the percentage yield was based on the grams of bismuth produced and on the grams of bismuth trichloride consumed in each run. Higher yield values undoubtedly would be realized on a larger scale with continuous operation since no efforts were made to account for the bismuth trichloride remaining in the cell at the end of each run. Loss of bismuth trichloride by volatilization, especially at the time of addition to the cell, was probably the major factor in reducing the percentage yield. Only a small amount of fuming was noted during electrolysis as long as the cell was covered; however, considerable fuming occurred when the molten bath was exposed to the atmosphere during the bismuth trichloride additions.

The power required for deposition of bismuth averaged 1.27 kwhr/lb of metal for the combined operations of electrolysis and bath temperature maintenance at approximately 400°C.

Since the anode was raised periodically to prevent short-circuiting, no effort was made to determine the anode current density precisely; however, approximate anode current densities were of the order of 200–300 amp/dm². At no time was the "anode effect" observed.

During the course of the experimental work the question of carbon content of the deposit was raised, since a graphite crucible was being used. No carbon analyses were obtained on the deposits; however, Griffith and Mallett (8) have shown that the solubility of carbon in bismuth varies with the temperature according to the equation $\log_{10}$wt % $C = -(360/T) - 3.17$. Taking 400°C as the temperature of operation, the deposited bismuth should have contained approximately 1 ppm of carbon.

Mathers (9) reported that bismuth deposits obtained from acidified aqueous bismuth trichloride solutions were contaminated with 0.3% chlorine. This contamination was explained on the basis of inclusion in the cathode deposit by adsorption, by precipitation as the basic salt, or by being discharged along with the metal from a complex cation, with some preference given to the latter view. Analysis of the bismuth obtained by fusion electrolysis of bismuth trichloride indicated the presence of 0.05% chlorine. Melting of the deposited bismuth with a sodium hydroxide flux, which is common practice in pyrometallurgical refining, reduced the chlorine content to 0.006%.

Spectrographic analysis of the deposits revealed only trace quantities of metallic impurities such as iron and copper. In view of the choice of electrolyte, special efforts were made to determine if any lithium had been codeposited with the bismuth. No lithium was detected spectrographically.

Conclusions

It has been shown that the solubility of bismuth in fused bismuth trichloride is reduced sufficiently by the use of a lithium chloride-potassium chloride eutectic mixture as a carrier salt to permit a feasible electrolysis to be carried out. Bismuth metal was deposited at an average current efficiency of 96% with an average yield of 88.8%. The power required for electrolysis and for maintaining the electrolyte molten was 1.27 kwhr/lb of bismuth. By plotting current values as a function of voltage, the decomposition potential of the electrolyte was determined to be 0.89 volt, at 420°C. The deposit was found to contain 0.05% chlorine, but this contamination was reduced to 0.006% by remelting the bismuth with a sodium hydroxide flux. Since bismuth is deposited in the liquid state, its removal from the cell can be accomplished by siphoning, and thus the process readily lends itself to continuous operation.

Acknowledgment

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Polarization in an Aluminum Reduction Cell

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ABSTRACT

A new method, which combines the technique of current reversal with the use of an a-c bridge, is presented for determining polarization in an aluminum reduction cell. Polarization was found to be composed of two parts. One part had a very short time constant and the other, a very long time constant.

Increasing the alumina concentration of the bath caused a large decrease in polarization. Vigorous agitation had the same effect. An increase in the NaF/AlF_3 ratio produced a moderate decrease in polarization, while an increase in the baking temperature of the anode produced a moderate increase in polarization. Additions of MgF_2, CaF_2, or SrF_2 had no noticeable effect on polarization. Polarization was found to increase with increasing current density, but the increase did not follow Tafel's law.

INTRODUCTION

Aluminum smelters are interested in electrolytic polarization of an aluminum reduction cell because polarization increases the cell voltage and thereby increases the power required to produce aluminum. Polarization is important also from a theoretical standpoint because an understanding of polarization may help in understanding the processes occurring in the cell. From the theoretical aspect, it would be desirable to separate anodic and cathodic polarization. This would require a stable reference electrode.

Both carbon and graphite were found to be unsatisfactory as reference electrodes since they did not give reproducible results. Piontelli and Montanelli (1) and Rempel and Khodak (2) used molten aluminum held in a corundum container as a reference electrode. This arrangement required the bath to be saturated with alumina. Since an important part of the present investigation was to be a study of the effect of alumina concentration in the bath, a corundum container could not be used. A study of the literature revealed no electrically insulating material that would not be attacked by molten cryolite. The container problem ruled out the silver-molten silver chloride reference electrode described by Senderoff and Brenner (3).

This lack of a suitable reference electrode eliminated the possibility of direct measurement of polarization, as well as making it impossible to separate anode and cathode polarization. However, there remained indirect methods that would allow the total cell polarization to be determined. The most common indirect methods of measuring polarization make use of current interruption, current reversal, or the superimposition of alternating current on direct current.

EXPERIMENTAL

Preliminary tests.—The method of current interruption was investigated first. A special circuit breaker permitted the breaking of up to 75 amp in less than 1/1000 sec. The circuit simultaneously triggered the sweep of a DuMont Model 304-A cathode ray oscillograph an instant before the current was interrupted and the voltage vs. time trace was photographed from the face of the oscillograph. These discharge curves were then analyzed by the method described by Busing and Kauzmann (4).

Two types of polarization with two very different time constants were found to be present simultaneously. The first type disappeared in much less than 1/1000 sec. The second type took several minutes to decay. Unfortunately, this method lacked the desired precision, largely because the inductance of the cell made the measurements of the part of polarization with the short time constant inaccurate.

Wohr (5) described a method of measuring cell resistance by superimposing, sequentially, alternating currents of two frequencies on the direct current and measuring the alternating currents and voltages through the cell. There will be considerable error in this method unless the direct current source is of high impedance since it represents a parallel path for the alternating current. At the frequencies recommended, the cell resistance obtained includes any short time constant polarization. If the measurements could be made at much higher frequencies, probably all polarization could be eliminated.

A combination of the bridge method, using superimposed alternating current and current reversal, was found more satisfactory. The modified method is easier to understand if the equivalent electrical circuit of the reduction cell derived from the preliminary tests is examined first.

Equivalent circuit.—Fig. 1 shows the equivalent circuit. Starting from left to right, E_d represents the decomposition potential, or the minimum voltage at which the overall cell reaction can take place. The voltage discharge curves indicated that E_d was about 1.2 v. However, rather large deviations from this value frequently occurred which could not be correlated with electrode condition, bath temperature, or bath composition. Nevertheless, 1.2 v agrees surprisingly well with the equilibrium reaction potential, 1.17 v, calculated from the free energy of the reaction $2Al_2O_3 + 3C = 4Al + 3CO_2$ at 980°C.

Next in Fig. 1 are two circuits, each composed of a variable resistor and variable capacitor in parallel. These represent polarization. One part of the polarization had a very short time constant and probably was caused by a gas

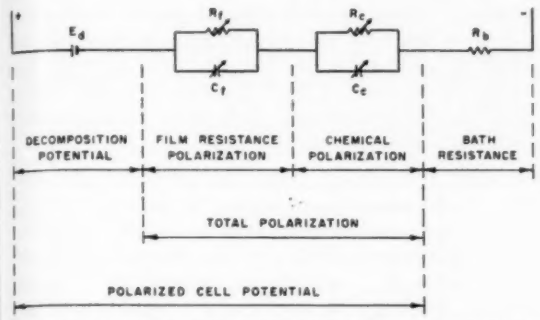

FIG. 1. Electrical equivalent circuit of aluminum reduction cell.

film on the anode, but might represent any adsorbed double layer. The resistance and capacitance associated with this polarization are referred to as R_f and C_f, respectively. The value of C_f was not determined, but was very small. The other part of the polarization had a very long time constant and is associated with R_c and C_c on the diagram. It was probably caused by the slowness of some step in the chemical reaction, but could be caused by any diffuse double layer or concentration gradient. The capacitance, C_c, increased with increasing current density, being about 0.05 farad at 50 amp. For simplicity, R_f will be referred to as film resistance and IR_c as chemical polarization.

Since the determination of E_d was inaccurate and some authorities question the reversibility of the reaction, the sum of E_d plus polarization will be referred to as the polarized cell potential. The polarized cell potential then equals $E_d + IR_f + IR_c$. While the equivalent circuit would indicate that there are only two factors involved in polarization, actually several factors having a long time constant may have been lumped together and several factors having a short time constant may have been lumped together.

The true ohmic resistance of the bath exclusive of electrode reactions is represented by R_b. For a constant temperature, bath composition and electrode composition, E_d and R_b are constant for a given cell. R_f, C_f, R_c and C_c are functions of current density.

Apparatus and procedure.—Electrolytic tests were conducted in graphite crucibles, 3 in. ID by 4¼ in. deep. An overflow hole was drilled at the 3.1 in. level. The crucibles were protected from oxidation by aluminum coated steel containers. Three hundred grams of the desired bath were added to the crucible. After the bath melted, 490 g of 99.95% aluminum (1095 grade) was added, providing a metal depth of 2.3 in. at the center, 1.3 in. at the edge, and an average depth of 1.85 in. The aluminum caused a small amount of bath to overflow, and in this way maintained a constant bath level. Actual bath compositions were determined by chemical analysis of a bath sample taken at the end of each test. The compositions stated are average values for each group. Individual analysis ranged ±1% from the average.

The anode immersion was controlled by lowering the anode by means of a screw adjustment until electrical contact was made, then lowering it 0.26 in. further. This gave a nominal anode area of 3 in.². Both the anode and cathode were provided with separate current and potential contacts. The current contact to the cathode was made through the bottom of the graphite crucible, while the cathode potential contact was made at the top edge of the crucible.

The anodes were made from a standard prebake anode mix, pressed into 1½ in. diameter electrodes, 1½ in. high, and baked at 1000°C (except when stated otherwise) for 24 hr at temperature. The cell was externally heated in an electric furnace, automatically controlled at 980°C. However, owing to the flow of current through the cell, the actual bath temperature fluctuated between 980° and 995°C. Temperatures were measured with Chromel-Alumel thermocouples with ±0.75% guaranteed accuracy.

The electrical circuit used is shown schematically in Fig. 2. It will be seen that the cell was in one leg of a Kelvin bridge circuit. A sine wave alternating current of 0.04 v rms was superimposed on the direct current to the cell. By turning the superimposed AC on and off and noting that no change in d-c voltage or current accompanied the change in AC, it was determined that the AC was not changing the cell characteristics. Use of 1020-cycle filters at the input to the oscillograph made the bridge sensitive to 1020 cycle AC only. Before each run, a preliminary adjustment of the Y axis phase control was made with a pure resistance substituted for the reduction cell. The oscillograph's X and Y inputs were made to agree in phase. When the cell was put in the circuit, balance was then indicated by a horizontal line. Resistive out of balance caused the line to slope up or down, while reactive out of balance caused the line to open into an ellipse.

Referring to Fig. 1, the bridge measures $R_b + R_f$ because, at 1020 cycles, C_c shunts R_c. Unfortunately, this bridge would not operate at frequencies high enough for C_f effectively to shunt R_f and allow determination of R_b. Therefore, the bath resistance was obtained by applying 6 amp of reversed polarity direct current to depolarize the cell. The a-c resistance measured on the bridge would fall with the application of reversed direct current. In a few seconds, a steady value was reached. This value was recorded as the bath resistance. After thus stabilizing, the value was independent of the reverse current from 0 to

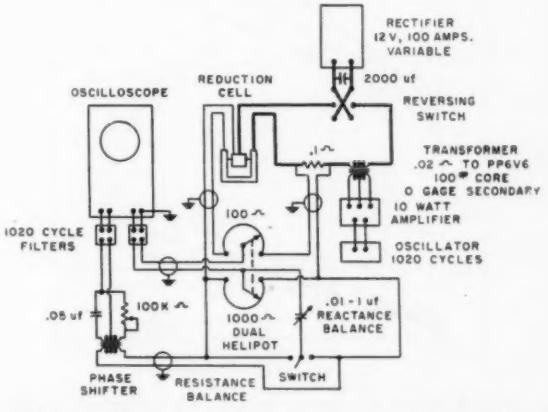

FIG. 2. Schematic wiring diagram of polarization test setup.

24 amp and increased only about 1% at 75 amp, indicating negligible reverse current polarization with a time constant less than 0.001 sec. A new anode was used for each determination to avoid the possibility that the reversed current had changed the anode permanently.

These measurements determined R_b, $R_b + R_f$, and the total cell voltage for each value of current. Subtracting IR_b from the total cell voltage gave the polarized cell potential. Subtracting R_b from $R_b + R_f$ gave the film resistance. Multiplying the film resistance by the current gave IR_f, the film resistance polarization. The mean values were reproducible to about ±0.1 v.

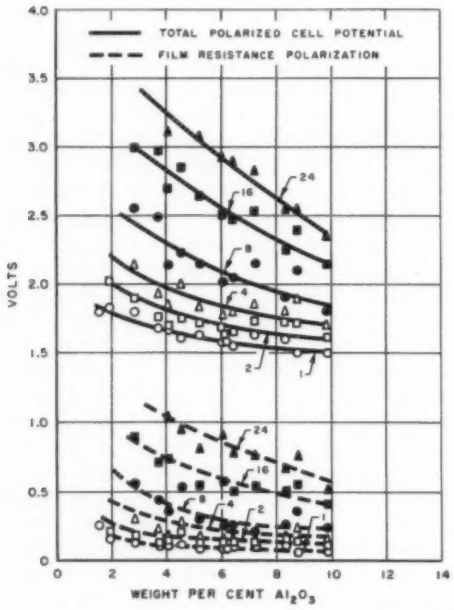

FIG. 3. Effect of Al_2O_3 concentration on polarization in Hall bath having a NaF/AlF_3 weight ratio = 1.47. Curve numbers indicate amp/in.² anode current density.

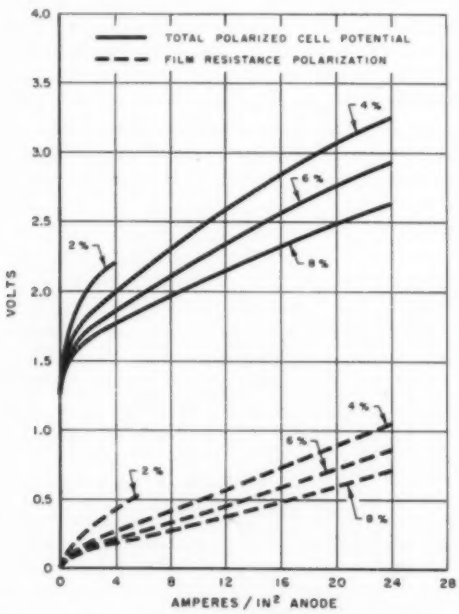

FIG. 4. Effect of current density on polarization in Hall bath having a NaF/AlF_3 weight ratio = 1.47. Curve numbers indicate % Al_2O_3 by weight in the bath.

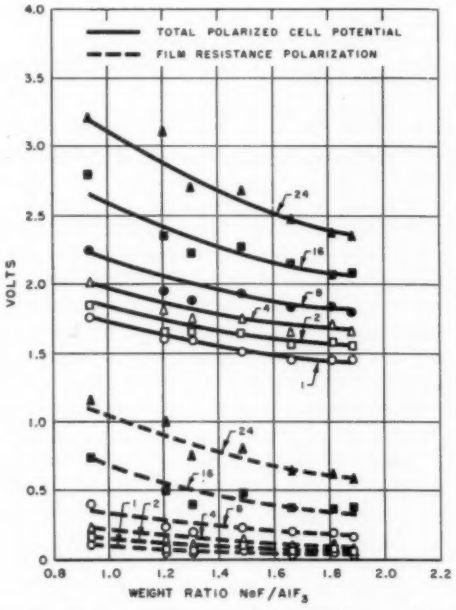

FIG. 5. Effect of bath ratio (NaF/AlF_3) on polarization in Hall bath containing 5.8% Al_2O_3. Curve numbers indicate amp/in.² anode current density.

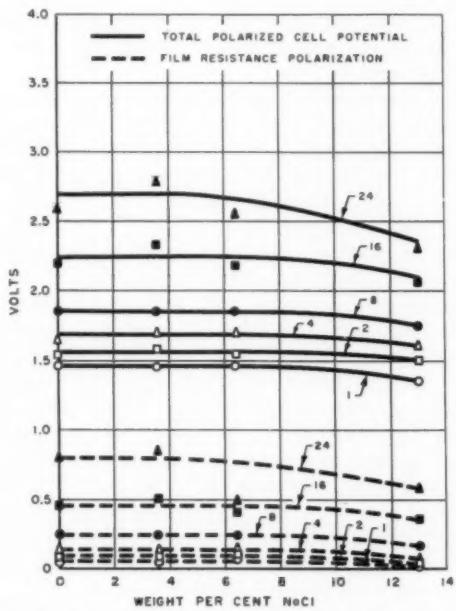

FIG. 6. Effect of sodium chloride on polarization in a cryolite bath having a NaF/AlF_3 weight ratio = 1.43 and containing 7.7% Al_2O_3. Curve numbers indicate amp/in.² anode current density.

Discussion of Results

These tests indicated that the largest factors affecting polarization were the alumina content of the bath and the current density. Fig. 3 presents the polarized cell potential as a family of curves at various anode current densities plotted against the alumina content of the bath. In all tests, the anode current density was about four times as great as the cathode current density. Unfortunately, this is a much greater ratio of anode to cathode current density than exists in a commercial cell. However, there seemed to be no way to avoid this discrepancy, for, if the anode were made larger, the current to the side walls would become excessive.

The current distribution over both the cathode and the anode must have been nonuniform because of the complex shape of the cathode. No means was found to avoid this difficulty. Nonuniform current distribution would cause the polarization to appear higher for a given nominal current density than it would be with a uniform current distribution. However, the effect could not have been very severe, for some of the results were checked in a large commercial cell having a quite uniform current distribution and were found to agree well.

The lower family of curves represents the part of polarization with a short time constant. A large decrease in both types of polarization with increasing alumina concentration is apparent. The effect is more marked at high current densities than at low current densities. The electrolytic baths in these tests contained cryolite plus 10% CaF_2, and had an average NaF/AlF_3 weight ratio of 1.47.

The data of Fig. 3 are replotted in Fig. 4 as a function of anode current density to show how polarization varies with current density. There is considerable deviation from Tafel's law (6) which states that the relationship between polarization voltage and current density is $E = a + b \log I$, where E is the polarization voltage, a and b are constants, and I is the current. Both the polarized cell potential and the film resistance polarization increased less with increasing currents than would be predicted by Tafel's law at low currents and more than would be predicted at high currents. Only above 4 amp/in.^{2} chemical polarization appeared to follow Tafel's law.

Fig. 5 shows that there was a moderate decrease in polarization with increasing NaF/AlF_3 ratios. These baths contained 10% CaF_2, 5.8% Al_2O_3, and Na_3AlF_6 plus NaF or AlF_3 to give the NaF/AlF_3 weight ratio indicated.

Sodium chloride had little effect on polarization at practical current densities. There was a moderate decrease in polarization with increasing NaCl concentration at very high current densities, as shown in Fig. 6. The bath was composed of cryolite, 7.7% alumina, and additions of NaCl. The NaF/AlF_3 ratio was 1.43. Other bath additions, namely KF up to 12%, MgF_2 up to 11%, CaF_2 up to 18%, and SrF_2 up to 10%, produced no significant effect on polarization.

Increasing the baking temperature of the anode over the normal range of practice caused a very slight increase in polarization. However, as shown in Fig. 7, use of graphite produced a fairly large increase in polarization. The bath used in these tests contained 6.7% Al_2O_3, 10% CaF_2, and cryolite, giving a NaF/AlF_3 ratio of 1.48.

Bath temperature was found to have an insignificant effect on polarization over the temperature range of 970°–1010°C, except at the highest current densities where there

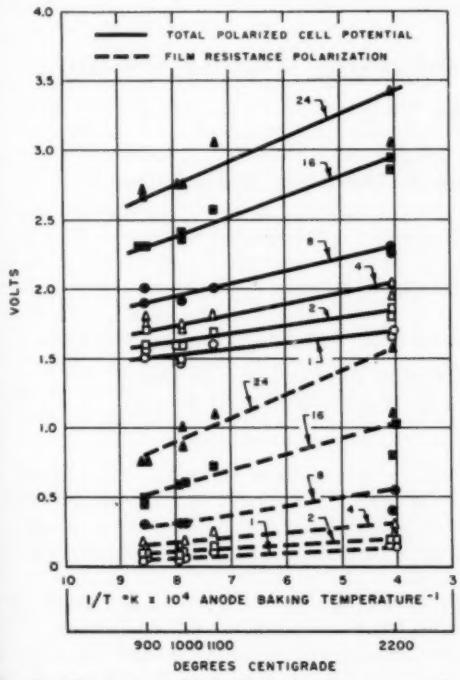

Fig. 7. Effect of anode baking temperature on polarization in Hall bath having a NaF/AlF_3 weight ratio = 1.48 and containing 6.7% Al_2O_3. Curve numbers indicate amp/in.^{2} anode current density.

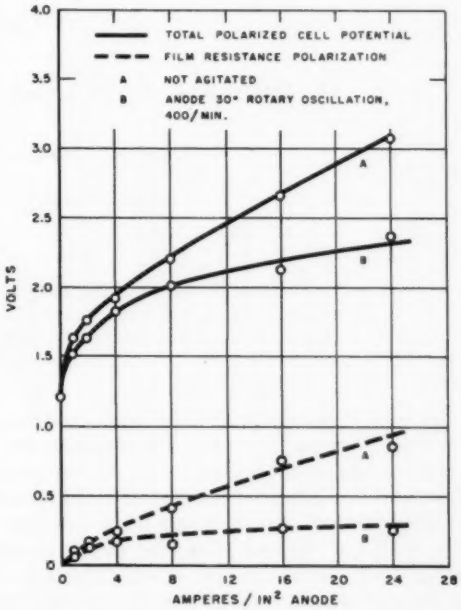

Fig. 8. Effect of agitation on polarization in Hall bath having a NaF/AlF_3 weight ratio = 1.48 and containing 5.2% Al_2O_3.

was a slight decrease in polarization with increasing temperature.

Polarization was reduced markedly by agitation. The most effective type of agitation investigated was a simple harmonic rotary oscillation of the anode through 30° at 400/min. The effect of rotary oscillation is shown in Fig. 8, for bath containing 10% CaF_2, 5.2% Al_2O_3, and cryolite, giving a NaF/AlF_3 ratio of 1.48.

There appears to be a close relationship between the ability of bath to wet carbon and polarization. Those additions which reduced polarization were observed also to improve the wetting of the carbon by the bath.

The author's measurements of polarized cell potential agree with measurements of Nozaki and Miyanchi (7) and Boner (8) who measured the average polarization on lines of commercial cells by the method of current interruption. Nozaki found the average polarized cell potential to be 1.72 v and Boner found 1.8 v for normal pot lines. Both values are within the range of the author's data which would compare with normal cell operation.

Probably the major portion of the polarization occurs at the anode. Rempel and Khodak (2) found extremely little polarization at the cathode. However, Piontelli and Montanelli (1) observed several tenths of a volt cathode polarization depending on bath composition. The total polarized cell potential calculated from data reported by Rempel and Khodak at 1.6 amp/in.^{2} in bath containing 4% excess AlF_3 and saturated with Al_2O_3 was 1.5 v. This agrees with the author's value of $E_d + IR_c$ under similar conditions. Apparently Rempel and Khodak did not include film resistance polarization. Piontelli and Montanelli reported only cathode polarization, so their results cannot be compared with this author's.

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1956 JOURNAL.

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Mechanisms of Hydrogen Producing Reactions on Palladium

II. Diffusion of Electrolytic Hydrogen through Palladium

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ABSTRACT

The rate of diffusion of hydrogen through several thicknesses of palladium for varying current densities was measured. The relationship between the diffusion current and the total polarizing current was established.

INTRODUCTION

It has been shown (1) that, under steady-state current flow, atomic hydrogen formed at a β-palladium cathode can produce molecular hydrogen both by the so-called catalytic and electrochemical mechanisms. If the palladium cathode is in the form of a diaphragm which separates two isolated bodies of solution, then the atomic hydrogen formed on the polarization side of the diaphragm may either be removed from this surface by the catalytic or electrochemical mechanism or it may diffuse through the metal and be removed from the back (diffusion) surface by catalytic combination. For such a diaphragm, production of molecular hydrogen may take place simultaneously on both surfaces or may favor either surface, depending on the relative rates of each hydrogen producing mechanism.

In this paper a study of the rates of diffusion of hydrogen through a palladium cathode-diaphragm is reported. Lewis and Ubbelohde (2) showed that they could get quantitative removal of hydrogen from palladium-hydrogen alloys by oxidation with ceric ion. In the present investigation, the rate of reduction of ceric ion on the dif-

fusion side of the diaphragm was used as a means of measuring the rate of flow of hydrogen through palladium. An application of these diffusion data in the investigation of the mechanisms of hydrogen producing reactions on palladium is given in Part III (3) of this series.

Experimental Method

The cell used in this study is shown in Fig. 1. It was constructed of Teflon; the solution capacity of each compartment was about 8 ml. The pre-electrolysis cathodes were platinum wires (0.05 in. diameter) which were pulled out of the solution (while the current was still passing) after pre-electrolysis was completed. The platinum electrodes were made of gauze; the reference electrodes were about 2 cm^2 in area and the electrodes used as anodes were about 18 cm^2. The palladium diaphragm (99.7%, annealed and hole-free) was mounted between two polyethylene washers and had an exposed area of 0.1413 cm^2. The cell compartment in which current passed between the Pt anode and the Pd cathode-diaphragm is referred to as the polarization compartment. The other compartment, in which there was no current flow, is called the diffusion compartment. The temperature was 37 ± 1°C.

Solution preparation (2*N* sulfuric acid) pre-electrolysis, and activation of the palladium cathode on the polarization side of the cell were done as previously reported (1). The diffusion side of the cell was filled with triply distilled water until preparation of the polarization side was completed. At that time the water in the diffusion compartment was replaced with a measured amount of a 0.12*N* ceric sulfate solution in 2*N* sulfuric acid. A rapid flow of purified hydrogen was passed through the polarization compartment. The diffusion side was stirred with a moderate flow of highly purified helium. Current was allowed to flow in the polarization compartment. After a ten-minute interval (in order to remove completely the dissolved oxygen in the diffusion compartment), a 0.600 ± 0.002 ml sample of ceric sulfate solution was removed from the diffusion compartment with a hypodermic syringe through the opening provided for the pre-electrolysis electrode. This sample was analyzed with standard ferrous ammonium sulfate using diphenylamine as an indicator. The titration was done with a Gilmont microburette which could be read to 0.001 ml.

For a particular run the current flow through the polarization side of the cell was set at a given value. The hydrogen overvoltage on the polarization side was determined. At the end of a 1000-sec interval a sample was removed from the diffusion compartment and analyzed for ceric ion. From six to eight successive 1000-sec determinations were made for each run. The remaining volume of the ceric sulfate solution was noted for each determination and the ceric ion concentration changes with time were converted to gram-equivalents of atomic hydrogen per second. Check runs were made for each current density value. Although the precision of the individual 1000-sec determinations of the rate of hydrogen flow through the diaphragm in any particular run was low (±35% of the mean value), the precision over the check runs was within 5%. This was because the successive determinations of hydrogen diffusion rates were self-compensating. Palladium diaphragms 0.001, 0.002, and 0.004 in. thick were used. At the end of a run the diaphragms were examined for holes by holding them against an intense light source in a dark room. Checks were made on several specimens by means of x-ray microradiographs. In only one case (0.0005 in. Pd) was the diaphragm punctured during a run. This run gave erratic results and the diaphragm was replaced.

The possibility of loss of hydrogen by diffusion from the edges of the palladium diaphragm was checked. This was done by carefully covering the edges of several specimens with molten polyethylene. These gave the same experimental results as diaphragms with uncovered edges. Examination of the covered edges at the end of a run showed no evidence of significant hydrogen loss from this source.

Results and Discussion

Fig. 2 shows the relationship between the per cent of hydrogen transmitted through palladium diaphragms of various thickness against the polarization current density. All of the current was used in the production of atomic hydrogen, part of which may have been removed as molecular hydrogen from the polarization side of the diaphragm and the remainder reacted with ceric ion on the diffusion side. The hydrogen transmitted through the diaphragm was calculated as a diffusion current density, j. This can be expressed by the equation:

$$i = i_p + j$$

where, i is the current density flowing to the palladium cathode, i_p is the equivalent current density representing

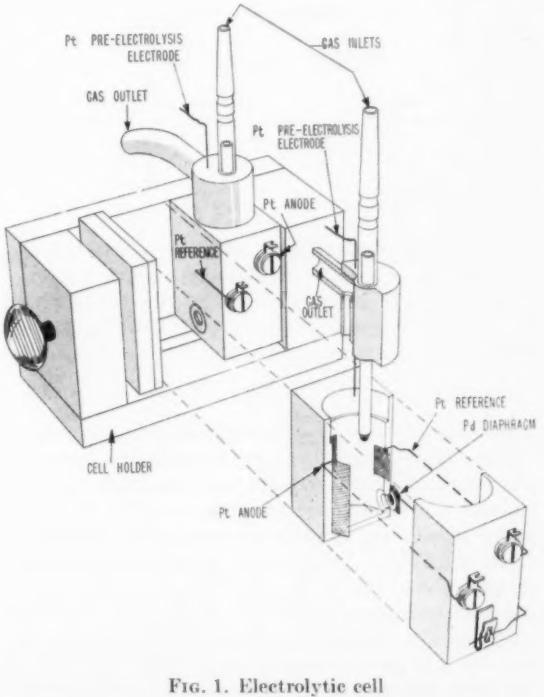

Fig. 1. Electrolytic cell

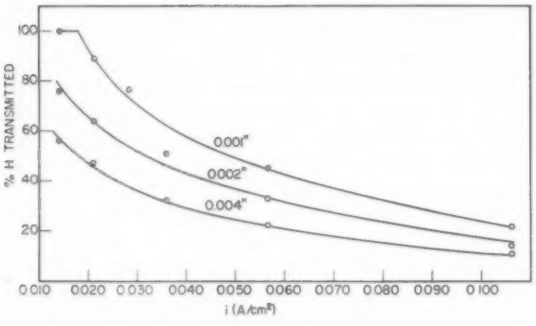

FIG. 2. Effect of current density on per cent hydrogen transmitted through palladium diaphragms of various thicknesses. The best possible fit of the points for the 0.001 in. curve indicated that 100% of the hydrogen was transmitted up to a current density of about 0.018 amp/cm².

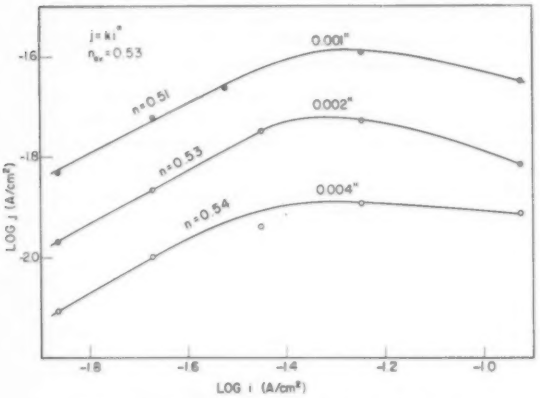

FIG. 3. Relationship between log i vs. log j

TABLE I. *Diffusion rates*

δ cm $< 10^3$	j_{max} g-eq. cm^{-2} sec^{-1} $\times 10^6$
2.54	13.26
5.08	9.70
10.16	6.64

molecular hydrogen evolution from the polarization surface, and j is the equivalent diffusion current density.

When log j is plotted against log i, the curves shown in Fig. 3 are obtained. These curves at the lower current densities show a linear portion which give the relationship:

$$j = Ki^{0.53}$$

Bodenstein (4) showed a $i^{\frac{1}{2}}$ relationship for the rate of diffusion of electrolytic hydrogen through iron. Barrer (5) and Heath (6), under certain conditions, show an $i^{\frac{1}{2}}$ relationship for palladium. At higher current densities j reaches a maximum and then declines slightly at the highest values of i. This j_{max} occurs at the current density at which the polarization side of the palladium approaches saturation with hydrogen (atomic ratio H/Pd $\sim$ 1). The phenomenon of saturation of palladium with hydrogen has been noted in the overvoltage studies of the authors (1, 3) and when this ratio of H/Pd is reached the overvoltage, η_p, of the polarization side becomes virtually independent of the current density. Thus, when the H/Pd ratio approaches unity, the hydrogen concentration of the palladium just under the surface layer of the polarization side reaches its maximum value. When this condition is reached, it has been shown (1) that a new electrode system sets in for which the catalytic properties are increased for the molecular-hydrogen-producing reaction. At current densities above this transition value, the removal of hydrogen by combination from the polarization surface of the palladium is so rapid that there appears to be a small decrease in the hydrogen concentration near this surface which results in a lowering of j. Barrer (5) at high current densities showed a transmission rate of electrolytic hydrogen through active palladium which was essentially independent of current density. However, a close examination of his data [(5) Fig. 4] indicates a small falling off of transmission rate with current density after the maximum j is reached.

The data shown in Table I indicate that the diffusion current, j_{max}, is inversely proportional to $\delta^{\frac{1}{2}}$ (where δ is the thickness of the Pd diaphragm) rather than to δ as required by Fick's first law. This means either that a surface reaction is an important factor in the rate-controlling process or that if the primary rate-determining step is diffusion of hydrogen through the palladium, then for this system the diffusion coefficient, D, is not a constant. The conclusion reached is that the latter condition prevails.

The reasons why the possibility of a retarded surface reaction determining the rate of j_{max} was eliminated are:

(*A*) Since at j_{max} the overvoltage on the polarization side of the palladium diaphragm is independent of current density, it was concluded (1) that the reactions on this side of the electrode are virtually at equilibrium and the activation energy required for the surface reactions is nearly equal to zero. Thus, the possibility of a retarded surface reaction on the polarization side is unlikely.

(*B*) Considering the surface reactions of the diffusion side of the palladium diaphragm, it is apparent that the reaction between the powerful reducing agent, adsorbed atomic hydrogen, and the strong oxidizing agent, ceric ion, would be extremely rapid and experimental observations by Lewis and Ubbelohde (2) and the authors have indicated that this is true. There would also be the possibility that a limiting diffusion current of ceric ions to the interface has been reached at j_{max}. But this possibility can be ruled out because j_{max} would not be an inverse function of the thickness of the palladium diaphragm; also, it would be fortuitous that j_{max} should occur at the point at which the overvoltage on the polarization side becomes independent of current density.

Experimental evidence indicates that hydrogen up to a H/Pd atomic ratio of 0.6 is dissolved as protons and above this it is dissolved differently (7, 9, 10). It is suggested that a possible explanation for the two solution mechanisms of hydrogen in palladium is as follows.

There are about 0.6 holes per atom in the d band of palladium. It was deduced (7), by magnetic susceptibility measurements, that up to an atomic ratio H/Pd $\sim$ 0.6 the dissolved hydrogen was completely ionized by giving up its electrons to the d bands. Additional evidence has

been given by nuclear magnetic resonance measurements (8). It is proposed that this amount of hydrogen is more or less strongly bound in the interior of the palladium electrode.

These measurements have also indicated that when H/Pd exceeds 0.6, the additional hydrogen is dissolved by a different mechanism. It is further proposed that hydrogen above the atomic ratio of 0.6 is dissolved as atomic hydrogen in the octahedral holes of the face-centered cubic lattice of the beta palladium.[1] The protons could be accommodated in either the tetrahedral or octahedral holes because of their very small size. Beta-palladium represents a closely packed system and, therefore, the hydrogen in the octahedral holes will be in relatively unstable positions. It is believed that this less firmly bound hydrogen is the hydrogen that diffuses through palladium and, because of the concentration gradient across the palladium, these hydrogen atoms will diffuse through the octahedral holes. This is in accord with the fact that it is impossible to prepare stable dried samples of palladium with more than 0.6 atomic ratio of dissolved hydrogen, and with the fact that the lattice constant increases linearly with the concentration of dissolved hydrogen (9) above this ratio.

[1] The effective radius of a tetrahedral hole is equal to $(a/2)\ [(3^{1/2}/2) - 2^{-1/2}]$; that of an octahedral hole is $(a/2)\ (1 - 2^{-1/2})$. Assuming a lattice constant, a, of 4.06Å, the effective radius of a tetrahedral hole is 0.322Å; that of an octahedral hole is 0.595Å. Since the effective radius of a hydrogen atom is 0.37Å, hydrogen atoms would most likely be accommodated in the octahedral holes.

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1956 Journal.

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Mechanism of Hydrogen Evolution at Tellurium Cathodes in Hydrochloric Acid

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ABSTRACT

Hydrogen overpotential at tellurium cathodes was studied in the concentration range 0.005*N*–5*N* aqueous hydrochloric acid at 30°C. The results indicated absence of specific adsorption. In dilute solutions a simple electrochemical mechanism, with two Tafel line slopes of 0.04 v and 0.12 v at 30°C, was established as the rate-determining mechanism. In concentrated solutions, a rate-determining dual electrochemical catalytic mechanism, with a slope of 0.06 v at 30°C, was suggested to explain the results in the low current density range. This dual mechanism changed to a simple one at high cathodic polarization.

Theoretical calculations of the Tafel line slopes for various dual mechanisms were also carried out. It was found that, for a dual slow discharge electrochemical mechanism or a dual slow discharge catalytic mechanism, the slope was exactly the same as that for the simple slow discharge, i.e., 0.12 v at 30°C.

The effect of neutral salts on hydrogen overpotential, η, at constant *p*H was studied. Addition of lanthanum chloride increased the numerical value of η at constant *p*H and current density. From the salt effect on η in 0.05*N* hydrochloric acid, the zeta potential was calculated and was found to have a value of *ca.* 0.05 v.

Introduction

Numerous researches have been carried out on the overpotential of metals (1), but overpotential studies on metalloids and nonmetals are very limited. Thus, Bowden and Rideal (2) studied the hydrogen overpotential on carbon cathodes and obtained a value of 0.84 v for the Tafel line slope.

The aim of the present investigation was to apply the experimental techniques of Bockris and co-workers (3), in order to calculate the parameters of the cathodic hydrogen evolution reaction on the metalloid tellurium.

Experimental

The electrolytic cell (Fig. 1*a*) was essentially similar to that of Bockris and Potter (4). However, it was necessary to separate the anode compartment *A* from the cathode compartment *B* by a third compartment *C*, in order to minimize the diffusion of gaseous anodic products toward the cathode. A sintered glass disk *D* was inserted between *C* and *B* for the same purpose. Compartment *C* was also used for the electrolytic purification of the solution. Water-sealed taps and ground glass joints were used to retard the diffusion of atmospheric oxygen into the cell.

The electrode[1] was in the form of a spectroscopically pure tellurium rod (7 mm diameter) with an apparent surface area of 4 cm². Since tellurium does not make a tight seal to glass, sublimes easily under heat, and its vapor combines with hydrogen to form tellurium hydride, the method involving heat treatment of the electrode in hydrogen (5) could not be used. The electrode was, however, fixed to glass in a manner shown by Fig. 1*b*. A thin tungsten wire, *a*, was tightly wrapped around one end of the tellurium rod, *b*. This end was squeezed inside a clean glass tubing, *c*, and the glass was sealed over the tungsten wire at *d*. The glass tubing was then sealed to the piston of a hypodermic syringe, whose barrel *E* (Fig. 1*a*) was fixed to the top of the cathode compartment of the electrolytic cell. The glass used for the electrode preparation was first cleaned with a mixture of A.R. nitric acid and A.R. sulfuric acid, followed by washing with conductance water ($K = 1 \times 10^{-6}$ mhos), and then dried in the flame. After being fixed into glass, the electrode was washed with conductance water and fixed in its position in the previously cleaned cell. Each electrode was used to trace one Tafel line only.

Appropriate conditions for the electrolytic purification of the solution were determined by successive increases in the amounts of pre-electrolysis until the overpotential remained constant (within ±10 mv) upon further increase. (2–3 times) of the extent of pre-electrolysis (3, 6). Preliminary experiments with a tellurium pre-electrolysis electrode had shown that this electrode disintegrated into black colloidal tellurium in solutions containing traces of oxygen. For this reason tellurium could not be used as a pre-electrolysis electrode, so a platinum electrode was used instead. Pre-electrolysis was carried out on the auxiliary platinum electrode (apparent surface area of 1 cm²) for about 20 hr using a current of 30–40 ma. These conditions were satisfactory to obtain reproducible results (within ±10 mv) in all solutions studied in the present investigation.

Hydrogen was purified from oxygen, carbon dioxide, and carbon monoxide in an all-glass apparatus (3). Hydrochloric acid solutions were prepared from the constant boiling acid. All glass parts of the apparatus were made of

[1] Prepared by Johnson and Matthey, Ltd., London, England.

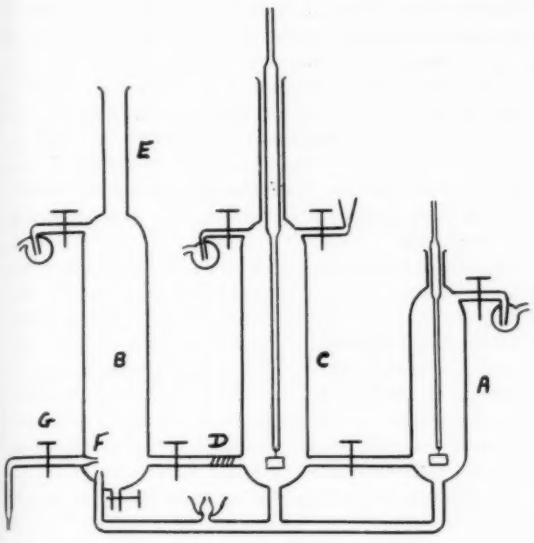

FIG. 1a. Electrode

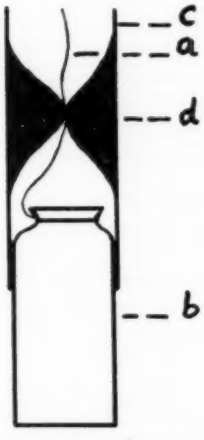

FIG. 1b. Electrolytic cell

hard borosilicate arsenic-free glass technically known as hysil.[2]

Before each run, the cell was cleaned with a mixture of A.R. nitric acid and A.R. sulfuric acid. This was followed by a thorough washing with conductance water. The cell was then fixed in its position, the electrode suspended in the cathode compartment, the cell filled with conductance water, the water displaced by pure hydrogen, the solution introduced and divided between the compartment *A* and *C* (Fig. 1*a*), and pre-electrolysis was begun by lowering the pre-electrolysis electrode, with a current of 30–40 ma imposed on it, into the solution in compartment *C*. After 20 hr, the pre-electrolysis electrode was drawn out of the solution, with the current still on, and part of the pre-electrolyzed solution in *C* was introduced into compartment *B* with a stream of hydrogen. The test tellurium electrode, with a current of 40 ma imposed on it, was then lowered into the solution and was adjusted to touch the tip of the Luggin capillary *F*.

A saturated calomel electrode, with a saturated KCl bridge (potential 238 mv at 30°C) was used as a reference electrode.

Diffusion of impurities from the salt bridge to the cathode compartment was hindered by keeping the level of the cathode compartment higher than the level of the salt bridge, and also by inserting a tap, *G*, between the Luggin, *F*, and the salt bridge (cf. Fig. 1*a*).

The direct method and the rapid technique (3) were employed, and the Tafel line was rapidly traced down to 10^{-6} amp/cm². The current was measured with a multirange millimicroammeter and the potential by a valve potentiometer. Temperature was kept constant with the aid of an air thermostat.

RESULTS

All results included in this section are the mean of six individual results which are reproducible among themselves to within ± 10 mv.

Fig. 2, 3, and 4 show the mean Tafel lines for tellurium cathodes in 5, 2, 1, 0.5, 0.3, and 0.1*N* aqueous hydrochloric acid between 10^{-6}–10^{-2} amp/cm² at 30°C. It is clear from these figures that Tafel lines obtained for tellurium cathodes in concentrations above 1*N* hydrochloric acid show a linear logarithmic section with one slope. However, Tafel lines in 1*N* hydrochloric acid and lower con-

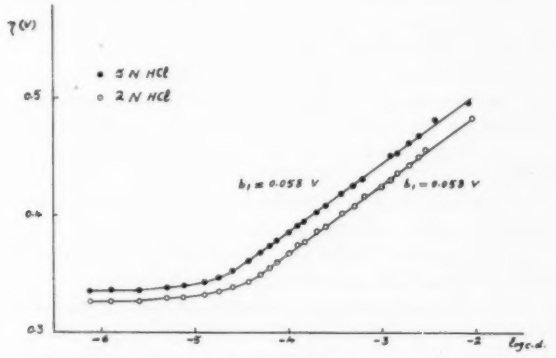

FIG. 2. Hydrogen overpotential on tellurium in 5*N* and 2*N* hydrochloric acid.

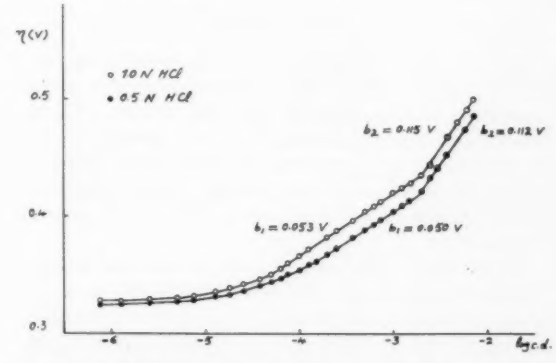

FIG. 3. Hydrogen overpotential on tellurium in 1.0*N* and 0.5*N* hydrochloric acid.

[2] Made by Chance Bros., Ltd., Birmingham, England.

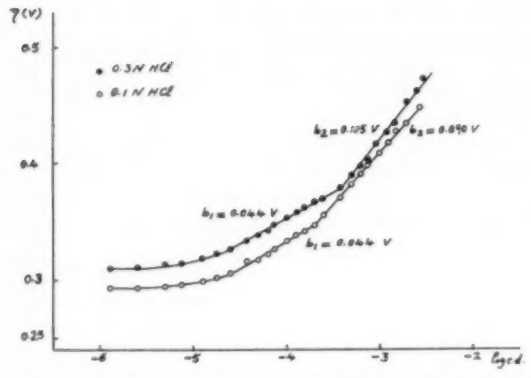

FIG. 4. Hydrogen overpotential on tellurium in 0.3*N* and 0.1*N* hydrochloric acid.

TABLE I

Conc.	b_1	b_2	η at 10^{-4}	Conc.	b_1	b_2	η at 10^{-4}
5.0*N*	58	—	386	0.1*N*	44	90	333
3.0*N*	51	—	380	0.05*N*	40	90	334
2.0*N*	58	—	368	0.03*N*	44	90	332
1.0*N*	53	115	365	0.02*N*	44	90	329
0.5*N*	50	112	354	0.01*N*	40	115	333
0.3*N*	44	105	352	0.005*N*	40	93	332

centrations clearly indicate the occurrence of two slopes in the linear logarithmic section. At comparatively low current densities, a region of stationary potential is obtained in all concentrations.

Table I contains the mean values of the slopes b_1 (at the low current density range) and b_2 (at the high current density range), together with the values of η at 10^{-4} amp/cm^2, for the various hydrochloric acid concentrations at 30°C.

Values of η (referred to the reversible hydrogen electrode), b_1, and b_2 are in millivolts.

It is clear from Table I that the overpotential is almost independent of *p*H, below 0.1*N* hydrochloric acid.

Fig. 5 shows the effect of adding an excess of lanthanum chloride (100 g/l HCl solution) on the Tafel line in 0.05*N* hydrochloric acid. It is clear from this figure that the neutral salt numerically increases η on tellurium cathodes in dilute solutions.

Discussion

The *p*H effect observed above 0.1*N* hydrochloric acid (cf. Table I) indicates a slight numerical increase of η with increase of concentration. Bockris and Conway (6) also observed a numerical increase of η with increase of concentration above 1*N* hydrochloric acid on silver cathodes, but the work of Jofa (7) on mercury clearly indicates a numerical decrease of η with increase of hydrochloric acid concentration.

The *p*H effect observed by Jofa (7) in high acid concentrations was attributed to the specific adsorption of anions as well as to the change of the activity coefficient of hydrogen ions in the double layer as compared with the bulk activity coefficient. Specific adsorption of anions resulted in the decrease of the overpotential values at low current densities. This caused an increase in the Tafel line slope at low current densities as compared with the slope at high current densities (7). Since this phenomenon was not observed in the present investigation on tellurium, it is possible to assume that specific adsorption of chloride ions does not occur on tellurium. The *p*H effect (cf. Table I) observed on tellurium in concentrated hydrochloric acid may thus be attributed to the change in the activity coefficient of hydrogen ions in the double layer as compared to the bulk value.

The occurrence of two slopes for the Tafel lines on silver in hydrochloric acid has been attributed by Bockris and Conway (6) to the specific adsorption of hydrogen ions. This causes the inflection of the Tafel lines to occur at increasingly low current densities, with increase of hydrochloric acid concentration (6). Since this is not the case with the results on tellurium (cf. Fig. 3 and 4), specific adsorption of cations cannot be the cause of change in slope for Tafel lines on tellurium.

From Table I it is clear that in dilute solutions (below 0.3*N*) the values of b_1 lie between 0.040 v and 0.044 v while those of b_2 lie between 0.090 v and 0.115 v. The occurrence of two slopes of $b_1 = 0.040$ v and $b_2 = 0.120$ v at 30°C indicates a simple electrochemical mechanism (8). This mechanism rquires that η be independent of *p*H, in absence of specific adsorption and under the conditions where Stern's theory applies (in dilute solutions). It can, therefore, be concluded that in solutions below 0.3*N* HCl the rate-determining step for hydrogen evolution on tellurium is the simple electrochemical mechanism, since η is independent of *p*H (cf. Table I).

Levina and Zarinskii (9) studied the effect of lanthanum chloride on hydrogen overpotential. Excess lanthanum ions compress the diffuse double layer and result in a value of zeta potential, ζ, very near to zero. The salt effect, at a constant current density and *p*H, for the simple electrochemical mechanism, in the region of the Tafel line with a slope of 0.040 v, is given by (8):

$$\eta = \text{constant} - \zeta/3 \qquad \text{(I)}$$

It is possible to use the above equation to evaluate ζ from hydrogen overpotential data. From Fig. 5, the value of η at 10^{-4} amp/cm^2 in presence of excess lanthanum chloride is -0.350 v in 0.05*N* hydrochloric acid. In absence of

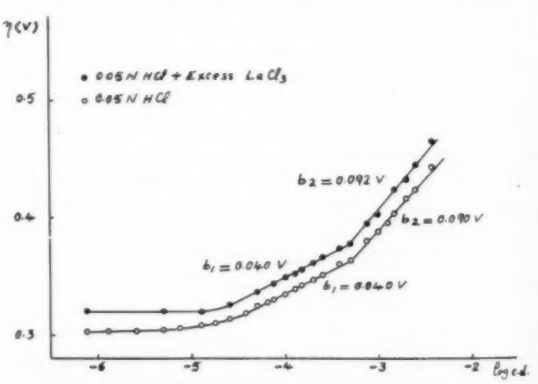

FIG. 5. Effect of excess lanthanum chloride on the hydrogen overpotential of tellurium in 0.05*N* hydrochloric acid.

lanthanum chloride, η at 10^{-4} amp/cm² is -0.335 v in the same hydrochloric acid concentration. Since in excess lanthanum chloride $\zeta = 0$, the constant in equation (I) is -0.350 v. Therefore, ζ is approximately 0.05 v. This result lies within the range of values for zeta potentials calculated by Frumkin (10) from hydrogen overpotential data on mercury.

Although results of the present investigation on tellurium in dilute (below 0.3N) hydrochloric acid are accounted for by the simple electrochemical mechanism, results in high acid concentrations cannot be explained by any of the simple mechanisms. Complex mechanisms were suggested by Kobozev and Nekrasov (11), by Lukovzew (12), and by Parsons (13) to explain the change of the slope of Tafel lines with cathodic polarization.

In the following discussion, the term "dual mechanism" is employed to cover the case when the rate of the over-all hydrogen evolution reaction is governed by two steps with nearly equal rates. The rates of the slow discharge step, V_1, of the electrochemical step V_2, and of the catalytic step, V_3, are given by (8):

$$V_1 = k_1 (1 - x)\, a_{H^+} \exp\left(-\frac{\Delta\phi F}{2RT}\right) \qquad \text{(II)}$$

$$V_2 = k_2(x \cdot 10^{-9}) a_{H^+} \exp\left(-\frac{\Delta\phi F}{2RT}\right) \qquad \text{(III)}$$

$$V_3 = k_3(x^2 \cdot 10^{-18}) \qquad \text{(IV)}$$

where k_1, k_2, and k_3 are rate constants, x is the coverage of the surface with adsorbed hydrogen atoms, a_{H^+} is the activity of hydrogen ions in the double layer, and $\Delta\phi$ is the galvanic potential difference between the Helmholtz double layer and the metal. Consider the following dual mechanisms.

1. A rate-determining dual slow discharge electrochemical mechanism, under the following condition:

$$V_1 \simeq V_2 \gg V_3 \qquad \text{(V)}$$

Substituting in (V) for V_1 and V_2 by their values as given by (II) and (III), the surface coverage, x, becomes:

$$x = k_1/(k_1 + k_2 \cdot 10^{-9}) \qquad \text{(VI)}$$

From equations (II) and (VI) or (III) and (VI), the net cathodic current at constant pH is given by:

$$i_c = \text{constant} \times \exp\left(-\frac{\Delta\phi F}{2RT}\right) \qquad \text{(VII)}$$

From (VII), it is clear that the slope of the Tafel line is equal to 0.120 v at 30°C, similar to that of the simple slow discharge mechanism and to that of the simple electrochemical mechanism at high cathodic polarization (8).

2. A rate-determining dual electrochemical catalytic mechanism (14), under the following condition:

$$V_1 \gg V_2 \simeq V_3 \qquad \text{(VIII)}$$

Substituting in (VIII) the values of V_2 and V_3 given by (III) and (IV), the surface coverage, x, becomes:

$$x = [k_2/(k_3 \cdot 10^{-9})] a_{H^+} \exp\left(-\frac{\Delta\phi F}{2RT}\right) \qquad \text{(IX)}$$

From (III) and (IX) or (IV) and (IX), the net cathodic current, at constant pH, is given by:

$$i_c = \text{constant} \times \exp\left(-\frac{\Delta\phi F}{RT}\right) \qquad \text{(X)}$$

Equation (X) clearly indicates that the Tafel line slope is 0.060 v at 30°C.

3. A rate-determining dual slow discharge catalytic mechanism, under the following conditions:

$$V_1 \simeq V_3 \gg V_2 \qquad \text{(XI)}$$

$$a_1(1 - x) = a_3 x^2 \qquad \text{(XII)}$$

where a_1 and a_3 [cf. ref. (8)] are given by:

$$a_1 = k_1(a_{H^+}) \exp\left(-\frac{\Delta\phi F}{2RT}\right) \qquad \text{(XIII)}$$

$$a_3 = k_3 \cdot 10^{-18} \qquad \text{(XIV)}$$

From (XII):

$$x = \frac{-a_1 + \sqrt{a_1(a_1 + 4a_3)}}{2a_3} \qquad \text{(XV)}$$

The solution of the above equation for x depends on the relative values of a_1 and a_3. Consider the following possibilities:

(i) $a_1 \gg a_3$. From (XV), the coverage becomes $x \simeq 0$.

(ii) $a_3 \gg a_1$. From (XIII), (XIV), and (XV), at constant pH, the surface coverage is given by:

$$x = \sqrt{\frac{a_1}{a_3}} = \text{constant} \cdot \exp\left(-\frac{\Delta\phi F}{4RT}\right) \qquad \text{(XVI)}$$

From (IV) and (XVI), the net cathodic current at constant pH becomes:

$$i_c = \text{constant} \cdot \exp\left(-\frac{\Delta\phi F}{2RT}\right) \qquad \text{(XVII)}$$

indicating a slope of 0.120 v at 30°C.

(iii) $a_1 \simeq a_3$. From (XII): $(1 - x) \simeq x^2$ and $x \simeq 0.62$. Substituting this value of x in equation (II), the net cathodic current is given by an equation similar to (XVII), and the slope of the Tafel line is 0.120 at 30°C.

Table II gives the possible values of the slope for the various rate-determining dual mechanisms at 30°C.

From the above discussion, it is clear that the results of hydrogen overpotential measurements on tellurium in concentrated (above 0.3N) hydrochloric acid, are best explained on the basis of a dual electrochemical catalytic mechanism, at the low current density range, probably changing to a simple electrochemical mechanism or a slow discharge mechanism at higher current densities (cf. Tables I and II). The fact that Tafel lines with only one slope are obtained in concentrations above 1N hydrochloric

TABLE II

Rate-determining mechanism	Slope (volt)
Dual slow discharge electrochemical	0.120
Dual electrochemical catalytic	0.060
Dual slow discharge catalytic	0.120

acid (cf. Table I and Fig. 2) might be explained by the assumption that the change of mechanism in such concentrations takes place at current densities higher than those used in this investigation.

At low current densities, the Tafel lines become parallel to the log current density axis at potentials negative with respect to the reversible hydrogen potential. This behavior is similar to that of nickel in acid solutions (15) at low current densities, and is similarly attributed to the dissolution of the cathode.

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Effect of the Walls of Electrolytic Cells on Current Distribution

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ABSTRACT

The field in the rectangular cell with two parallel and flat plates as electrodes has been analyzed. In this paper, no consideration is given to polarization phenomena for mathematical convenience.

As a numerical example, current distribution at the surface of the electrode has been calculated in detail for the special case where distance between electrodes equals cell width. Moreover, diagrams are given to show numerical relations such as the ratio of current on inner and outer surfaces, total current distribution over the electrodes, etc., for the general case.

INTRODUCTION

Lately much attention has been given to the design of electrolytic cells in the field of chemical engineering; one of the most important problems is the distribution of potential or current in such cells. No basic solution has yet been attained in spite of many efforts, e.g., Kasper (1), Wagner (2), and others, partly because of difficulties due to polarization phenomena near the surface of electrodes.

Analysis of the electric field is one of the fundamental problems involved, and special attention must be paid eventually to polarization phenomena. For mathematical simplicity, the effect of polarization is neglected in the present paper. This approximation is made regretfully, but it is believed that the results will nevertheless be suggestive in many respects.

Another difficulty is the fact that the domain of the electric field under consideration is limited by the electrolytic cell. If the field were unrestricted in all directions, analysis would be much simpler; but in the case of parallel-plate electrodes in a rectangular electrolyzer, which is the usual type of bath in electrochemistry and in the electrochemical industry, the mathematical treatment becomes very difficult.

In the following, the problem is treated as a two-dimensional one, and the Schwarz-Christoffel transformation is used. If the effects of four walls in a rectangular cell are considered, a hyper-elliptic integral appears, and the analysis is beyond possibility. Therefore, another model must be employed.

It is known from experience that the walls facing the back of electrodes have relatively small influence on the distribution of potential and current, especially when the electrodes extend close to the side walls. Accordingly, the present treatment considers only the effect of the side

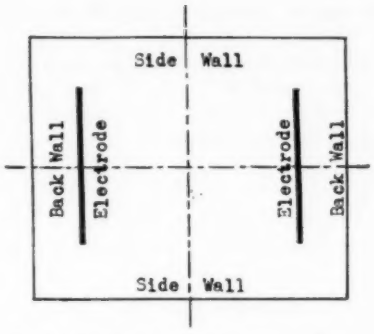

FIG. 1. Profile of the rectangular bath

walls on the current distribution and assumes that the back walls are far removed from the electrodes.

MATHEMATICAL METHOD

Applying the above-mentioned assumptions, the model in Fig. 1 can be represented by the z-plane of Fig. 2. Applying the methods of conformal mapping, the interior of the polygon (OA′B′C′H′RHCBAO) formed at the upper half of this z-plane can be transformed on the upper half of the t-plane. Here, 2α, 2β, and 2γ are the distances between the electrodes, the width of the electrodes and of the cell, respectively.

The transformation from the z-plane to the t-plane can be made by the equation

$$\frac{dz}{dt} = M \frac{t^2 - b^2}{\sqrt{t^2 - a^2}\sqrt{t^2 - c^2}\,(t^2 - h^2)} \qquad [1]$$

where M is a constant and a, b, c, and h are also constants corresponding to the positions of the points A, B, C, and H on the t-plane, respectively.

Using the equation (6)

$$t^2 = \mathcal{P}(s) - e_3 \qquad [2]$$

the t-plane is transformed within the rectangle of the s-plane with $2\omega_1$ and ω_3/i as the lengths of its adjacent sides. If, of the two periods $2\omega_1$ and $2\omega_3$ of the Weierstrass $\mathcal{P}$-function, $\mathcal{P}(s)$, the former is a real number, then the latter is purely imaginary, and $\omega_1 > 0$, $\omega_3/i > 0$. Therefore, from equations [1] and [2] and the use of the relation

$$\mathcal{P}'(s) = -2\sqrt{\mathcal{P}(s) - e_1}\sqrt{\mathcal{P}(s) - e_2}\sqrt{\mathcal{P}(s) - e_3}$$

one obtains

$$\frac{dz}{ds} = M \frac{-\{\mathcal{P}(s) - \mathcal{P}(\mu)\}\mathcal{P}'(s)}{2\sqrt{\mathcal{P}(s) - e_1}\sqrt{\mathcal{P}(s) - e_2}\sqrt{\mathcal{P}(s) - e_3} \cdot \{\mathcal{P}(s) - \mathcal{P}(\nu)\}} \qquad [3]$$

$$= M \frac{\mathcal{P}(s) - \mathcal{P}(\mu)}{\mathcal{P}(s) - \mathcal{P}(\nu)}$$

Here, μ and ν are the coordinates of the points B and H on the s-plane, respectively; e_j stands for $\mathcal{P}(\omega_j)$, with $j = 1, 2, 3$.

This result coincides with the relation derived by Sasaki and others in their research on the lift of an aerofoil placed near a plane wall (3–5).

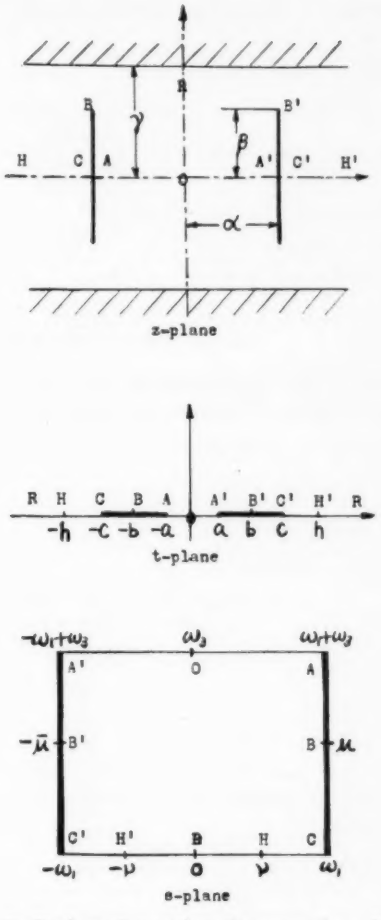

FIG. 2. Conformal mappings between the original, the parametric, and the potential planes.

Employing the addition formula of the Weierstrass ζ-function

$$\frac{\mathcal{P}'(u)}{\mathcal{P}(u) - \mathcal{P}(v)} = \zeta(u - v) + \zeta(u + v) - 2\zeta(u)$$

one finds from equation [3]:

$$\frac{dz}{ds} = M \frac{\mathcal{P}(\nu) - \mathcal{P}(\mu)}{\mathcal{P}'(\nu)} [\zeta(\mu + \nu) - \zeta(\mu - \nu) - \zeta(s + \nu) + \zeta(s - \nu)] \qquad [4]$$

Considering the relation

$$\zeta(u) = \frac{d}{du} \log \sigma(u) \qquad [5]$$

there is obtained:

$$z = M \frac{\mathcal{P}(\nu) - \mathcal{P}(\mu)}{\mathcal{P}'(\nu)} \cdot \left[\{\zeta(\mu + \nu) - \zeta(\mu - \nu)\}s - \log \frac{\sigma(s + \nu)}{\sigma(s - \nu)}\right] + C \qquad [6]$$

To determine the integration constant C, make $z = 0$ and $s = \omega_3$:

$$0 = M\frac{\mathcal{P}(v) - \mathcal{P}(\mu)}{\mathcal{P}'(v)} \cdot \left[\{\zeta(\mu + v) - \zeta(\mu - v)\}\omega_3 - \log\frac{\sigma(\omega_3 + v)}{\sigma(\omega_3 - v)}\right] + C \quad [7]$$

Substituting equation [7] into equation [6]

$$z = M\frac{\mathcal{P}(v) - \mathcal{P}(\mu)}{\mathcal{P}'(v)}\left[\{\zeta(\mu + v) - \zeta(\mu - v)\}(s - \omega_3) - \log\frac{\sigma(s + v)\sigma(\omega_3 - v)}{\sigma(s - v)\sigma(\omega_3 + v)}\right] \quad [8]$$

The constant M can now be obtained. The following relations concerning the σ-functions are available (6)

$$\sigma(u \pm \omega_j) = \pm e^{\pm\eta_j u}\sigma(\omega_j)\sigma_j(u), \qquad j = 1, 2, 3 \quad [9]$$

and

$$\log\frac{\sigma(\omega_1 + \omega_3 + v)\sigma(\omega_3 - v)}{\sigma(\omega_1 + \omega_3 - v)\sigma(\omega_3 + v)} = \log\frac{\sigma(v - \omega_2)\sigma(v - \omega_3)}{\sigma(v + \omega_2)\sigma(v + \omega_3)} = -2v(\eta_2 + \eta_3) = 2v\eta_1 \quad [10]$$

where

$$\eta_j = \zeta(\omega_j)$$

Substituting the coordinates of the point $A(z = -\alpha, s = \omega_1 + \omega_3)$ into equation [8], and considering the above relations, one has

$$-\alpha = M\frac{\mathcal{P}(v) - \mathcal{P}(\mu)}{\mathcal{P}'(v)} \cdot [\{\zeta(\mu + v) - \zeta(\mu - v)\}\omega_1 - 2v\eta_1] \quad [11]$$

On the other hand, as $z = -\alpha$ and $s = \omega_1$ at the point C, equation [8] becomes

$$-\alpha = M\frac{\mathcal{P}(v) - \mathcal{P}(\mu)}{\mathcal{P}'(v)} \cdot [\{\zeta(\mu + v) - \zeta(\mu - v)\}(\omega_1 - \omega_3) - 2v(\eta_1 - \eta_3)] \quad [12]$$

because from equations [9] and [10],

$$\log\frac{\sigma(\omega_1 + v)\sigma(\omega_3 - v)}{\sigma(\omega_1 - v)\sigma(\omega_3 + v)} = \log\frac{\sigma(v + \omega_1)\sigma(v - \omega_3)}{\sigma(v - \omega_1)\sigma(v + \omega_3)} = 2v(\eta_1 - \eta_3) \quad [13]$$

Consequently, from equations [11] and [12], one obtains

$$M\frac{\mathcal{P}(v) - \mathcal{P}(\mu)}{\mathcal{P}'(v)}[\{\zeta(\mu + v) - \zeta(\mu - v)\}\omega_3 - 2v\eta_3] = 0 \quad [14]$$

As it is clear that

$$M\frac{\mathcal{P}(v) - \mathcal{P}(\mu)}{\mathcal{P}'(v)} \neq 0$$

it follows from equation [14] that,

$$\zeta(\mu + v) - \zeta(\mu - v) = \frac{2v\eta_3}{\omega_3} \quad [15]$$

Next, the sign of $M[\mathcal{P}(v) - \mathcal{P}(\mu)/\mathcal{P}'(v)]$ must be considered.

If one considers the domain, $c < t < h$, in equation [1], it will be clear that $dz/dt > 0$, $t^2 - b^2 > 0$, $\sqrt{t^2 - a^2} > 0$, $\sqrt{t^2 - c^2} > 0$ and $t^2 - h^2 < 0$, and accordingly, $M < 0$. Consequently from the relation

$$\mathcal{P}'(v) = -z\sqrt{\mathcal{P}(v) - e_1}\sqrt{\mathcal{P}(v) - e_2}\sqrt{\mathcal{P}(v) - e_3} \quad [16]$$

it can be concluded that $\mathcal{P}'(v) < 0$ if $0 < v < \omega_1$.

The $\mathcal{P}$-function can be represented by ϑ-functions that is,

$$\mathcal{P}(u) = e_j + \frac{1}{4\omega_1^2}\left[\frac{\vartheta_1'(0)}{\vartheta_{j+1}(0)}\right]^2\left[\frac{\vartheta_{j+1}(v)}{\vartheta_1(v)}\right]^2, \quad j = 1, 2, 3 \quad [17]$$

where ϑ_j represents the families of the ϑ-function, and $v = u/2\omega_1$. Putting

$$v_1 = \frac{v}{2\omega_1} \quad [18]$$

$$\mu_1 = \frac{\mu}{2\omega_1} \quad [19]$$

and

$$\mu = \omega_1 + i\mu'' \quad [20]$$

equation [17] yields

$$\mathcal{P}(v) - \mathcal{P}(\mu) = \frac{1}{4\omega_1^2}\left[\frac{\vartheta_1'(0)}{\vartheta_{j+1}(0)}\right]^2 \cdot \left\{\left[\frac{\vartheta_{j+1}(\xi_1)}{\vartheta_1(v_1)}\right]^2 - \left[\frac{\vartheta_{j+1}(\mu_1)}{\vartheta_1(\mu_1)}\right]^2\right\} \quad [21]$$

In equation [21] it is known that

$$\frac{1}{4\omega_1^2}\left[\frac{\vartheta_1'(0)}{\vartheta_{j+1}(0)}\right]^2 > 0$$

so, the sign of the left hand side of equation [21] is the same as that of the bracket $\{\}$. For instance, if $j = 1$, one has

$$\left[\frac{\vartheta_2(v_1)}{\vartheta_1(v_1)}\right]^2 - \left[\frac{\vartheta_2(\mu_1)}{\vartheta_1(\mu_1)}\right]^2 = \left[\frac{\vartheta_2(v_1)}{\vartheta_1(v_1)}\right]^2 + \left[\frac{\vartheta_1\left(\frac{i\mu_1''}{\tau}\middle| -\frac{1}{\tau}\right)}{\vartheta_4\left(\frac{i\mu_1''}{\tau}\middle| -\frac{1}{\tau}\right)}\right]^2 > 0 \quad [22]$$

If it is considered that (7)

$$\vartheta(iv + \tfrac{1}{2}\pi) = \vartheta_2(iv) \quad [23]$$

$$\vartheta_2(iv + \tfrac{1}{2}\pi) = -\vartheta_1(iv) \quad [24]$$

then

$$\vartheta_1(iv\,|\,\tau) = i\sqrt{\frac{i}{\tau}}\,e^{v^2\pi i/\tau}\vartheta_1\left(\frac{iv}{\tau}\middle| -\frac{1}{\tau}\right) \quad [25]$$

and

$$\vartheta_2(iv\,|\,\tau) = i\sqrt{\frac{i}{\tau}}\,e^{v^2\pi i/\tau}\vartheta_4\left(\frac{iv}{\tau}\middle| -\frac{1}{\tau}\right) \quad [26]$$

Therefore,

$$\mathcal{P}(\nu) - \mathcal{P}(\mu) > 0 \qquad [27]$$

and

$$M \frac{\mathcal{P}(\nu) - \mathcal{P}(\mu)}{\mathcal{P}'(\nu)} > 0 \qquad [28]$$

Consequently, equation [8] can be expressed as

$$z = M \frac{\mathcal{P}(\nu) - \mathcal{P}(\mu)}{\mathcal{P}'(\nu)} \cdot \left[\frac{2\nu\eta_3}{\omega_3} (s - \omega_3) + \log \frac{\sigma(s - \nu)}{\sigma(s + \nu)} \frac{\sigma(\omega_3 + \nu)}{\sigma(\omega_3 - \nu)} \right] \qquad [29]$$

in which the first term has been rewritten by substituting the relation stated in equation [15]. Moreover, at the point R, $z = i\gamma$, $s = 0$, and

$$\log \frac{\sigma(-\nu)}{\sigma(\nu)} \frac{\sigma(\omega_3 + \nu)}{\sigma(\omega_3 - \nu)} = \log \frac{\sigma(\nu + \omega_3)}{\sigma(\nu - \omega_3)} = i\pi + 2\nu\eta_3$$

Consequently, from equation [29]

$$M \frac{\mathcal{P}(\nu) - \mathcal{P}(\mu)}{\mathcal{P}'(\nu)} = \frac{\gamma}{\pi} \qquad [30]$$

By substituting this into equation [29], one has,

$$z = \frac{\gamma}{\pi} \left[\frac{2\nu\eta_3}{\omega_3} (s - \omega_3) + \log \frac{\sigma(s - \nu)}{\sigma(s + \nu)} \frac{\sigma(\omega_3 + \nu)}{\sigma(\omega_3 - \nu)} \right] \qquad [31]$$

while substitution of equation [30] into equation [11] yields

$$-\alpha = \frac{\gamma}{\pi} \left[2 \frac{\nu\eta_3}{\omega_3} \omega_1 - 2\nu\eta_1 \right] = -\frac{\gamma}{\pi} \frac{2\nu}{\omega_1} [\eta_1\omega_3 - \eta_3\omega_1]$$

If the Legendre relation

$$\eta_1\omega_3 - \eta_3\omega_1 = \pi/2$$

is applied, one obtains

$$\nu = \frac{\alpha}{\gamma} \frac{\omega_3}{i} \qquad [32]$$

Next the value of μ must be determined. Employing the relations $z = -\alpha + i\beta$ and $s = \mu$ at the point B, the following equation is derived from equation [31]

$$-\alpha + i\beta = \frac{\gamma}{\pi} \left[\frac{2\nu\eta_3}{\omega_3} (\mu - \omega_3) + \log \frac{\sigma(\mu - \nu)}{\sigma(\mu + \nu)} \frac{\sigma(\omega_3 + \nu)}{\sigma(\omega_3 - \nu)} \right] \qquad [33]$$

Thus, equations [15], [32], and [33] yield the constants ω_3, ν, and η. Because of the uniform distribution of potential, as is clear from the nature of the s-plane in Fig. 2, equation [31] indicates directly the relation between the original plane and the potential plane. It gives the potential function, $s = f(z)$, of the electric field, which is depicted in the z-plane and may be obtained by solving equation [31]. The next step is to expand these equations into the theta function $\vartheta(v)$, for the sake of convenience in numerical calculations.

Expression by the Theta Functions

In the first place, the addition theorem of the ζ-function, applied to equation [15], leads to

$$2\zeta(\nu) + \frac{\mathcal{P}'(\nu)}{\mathcal{P}(\nu) - \mathcal{P}(\mu)} = \frac{2\nu\eta_3}{\omega_3} \qquad [34]$$

On combining the following relation (8)

$$\zeta(u) = \frac{\eta_1 u}{\omega_1} + \frac{1}{2\omega_1} \frac{\vartheta_1'(v)}{\vartheta_1(v)} \qquad [35]$$

with the Legendre relation, $\eta_1\omega_3 - \eta_3\omega_1 = \pi/2$, one obtains

$$2\zeta(\nu) - \frac{2\nu\eta_3}{\omega_3} = \frac{\pi}{\omega_1} \left\{ \frac{\alpha}{\gamma} + \frac{1}{\pi} \frac{\vartheta_1'(\nu_1)}{\vartheta_1(\nu_1)} \right\} \qquad [36]$$

On the other hand, from the relation (9)

$$\mathcal{P}'(\nu) = -\frac{\pi}{4\omega_1^3} [\vartheta_1'(0)]^2 \frac{\vartheta_2(\nu_1) \cdot \vartheta_3(\nu_1) \cdot \vartheta_4(\nu_1)}{[\vartheta_1(\nu_1)]^3} \qquad [37]$$

and equation [21], one gets

$$\frac{\mathcal{P}'(\nu)}{\mathcal{P}(\nu) - \mathcal{P}(\mu)} = -\frac{\pi}{\omega_1} [\vartheta_1'(0)]^2 \frac{\vartheta_2(\nu_1) \cdot \vartheta_3(\nu_1) \cdot \vartheta_4(\nu_1)}{[\vartheta_1(\nu_1)]^3} \frac{1}{\left[\frac{\vartheta_2(\nu_1)}{\vartheta_1(\nu_1)}\right]^2 + \left[\frac{\frac{1}{i}\vartheta_1(i\mu_1'')}{\vartheta_2(i\mu_1'')}\right]^2} \qquad [38]$$

Substituting equations [36] and [38] into equation [34], and solving for the term $[1/i\vartheta_1(i\mu_1'')/\vartheta_2(i\mu_1'')]^2$:

$$\left[\frac{1/i\vartheta_1(i\mu_1'')}{\vartheta_2(i\mu_1'')}\right]^2 = \frac{\vartheta_2(\nu_1)}{[\vartheta_1(\nu_1)]^3} \frac{1}{\alpha/\gamma + \frac{1}{\pi}\frac{\vartheta_1'(\nu_1)}{\vartheta_1(\nu_1)}} \left\{ [\vartheta_2(0)]^2 \cdot \vartheta_3(\nu_1) \cdot \vartheta_4(\nu_1) - \vartheta_1(\nu_1) \cdot \vartheta_2(\nu_1) \cdot \left[\frac{\alpha}{\gamma} + \frac{1}{\pi} \frac{\vartheta_1'(\nu_1)}{\vartheta_1(\nu_1)} \right] \right\} \qquad [39]$$

In the next place, consider the expansion of equation [33]. Introducing the well-known relation

$$\sigma(u \pm \omega_j) = \pm e^{\pm\eta_j u} \sigma(\omega_j) \cdot \sigma_j(u), \qquad j = 1, 2, 3 \qquad [40]$$

one obtains

$$\frac{\sigma(\mu - \nu)}{\sigma(\mu + \nu)} = \frac{\sigma(\nu - i\mu'' - \omega_1)}{\sigma(\nu + i\mu'' + \omega_1)} \frac{\sigma(\nu + \omega_3)}{\sigma(\nu - \omega_3)} = e^{-2\nu(\eta_1 - \eta_3)} \frac{\sigma_1(\nu - i\mu'')}{\sigma_1(\nu + i\mu'')} \qquad [41]$$

Furthermore, since (10)

$$\sigma_1(u) = \frac{\vartheta_2(v)}{\vartheta_2(0)} e^{2\eta_1\omega_1 v^2} = \frac{\vartheta_2(v)}{\vartheta_2(0)} e^{\eta_1 u^2/2\omega_1} \qquad [42]$$

it is found that

$$\frac{\sigma_1(\nu - i\mu'')}{\sigma_1(\nu + i\mu'')} = e^{-i2\eta_1\nu\mu''/\omega_1} \frac{\vartheta_2(\nu_1 - i\mu_1'')}{\vartheta_2(\nu_1 + i\mu_1'')} \qquad [43]$$

Moreover, the ϑ-function may be represented by infinite products as follows (11)

$$\frac{\vartheta_2(\nu_1 - i\mu_1'')}{\vartheta_2(\nu_1 + i\mu_1'')} = \frac{\cos \pi(\nu_1 - i\mu_1'')}{\cos \pi(\nu_1 + i\mu_1'')} \frac{\prod_{n=1}^{\infty} \{1 + 2q^{2n} \cos 2\pi(\nu_1 - i\mu_1'') + q^{4n}\}}{\prod_{n=1}^{\infty} \{1 + 2q^{2n} \cos 2\pi(\nu_1 + i\mu_1'') + q^{4n}\}} \qquad [44]$$

Considering the relation

$$\log \frac{a+ib}{a-ib} = i \cdot 2 \tan^{-1} \frac{b}{a} \qquad [45]$$

the logarithm of equation [44] becomes

$$\log \frac{\vartheta_2(\nu_1 - i\mu_1'')}{\vartheta_2(\nu_1 + i\mu_1'')} = i \cdot 2 \tan^{-1}\left(\tan \frac{\pi\nu}{2\omega_1} \cdot \tanh \frac{\pi\mu''}{2\omega_1}\right)$$
$$+ i \cdot 2 \sum_{n=1}^{\infty} \tan^{-1}\left(\frac{2q^{2n} \sin \frac{\pi\nu}{\omega_1} \cdot \sinh \frac{\pi\mu''}{\omega_1}}{1 + 2q^{2n} \cos \frac{\pi\nu}{\omega_1} \cdot \cosh \frac{\pi\mu''}{\omega_1} + q^{4n}}\right) \qquad [46]$$

Substituting this equation into equation [43], one has

$$\log \frac{\sigma_1(\nu - i\mu'')}{\sigma_1(\nu + i\mu'')} = -i \frac{2\eta_1 \nu \mu''}{\omega_1}$$
$$+ i \cdot 2 \tan^{-1}\left(\tan \frac{\pi\nu}{2\omega_1} \cdot \tanh \frac{\pi\mu''}{2\omega_1}\right) \qquad [47]$$
$$+ i \cdot 2 \sum_{n=1}^{\infty} \tan^{-1}\left(\frac{2q^{2n} \sin \frac{\pi\nu}{\omega_1} \cdot \sinh \frac{\pi\mu''}{\omega_1}}{1 + 2q^{2n} \cos \frac{\pi\nu}{\omega_1} \cdot \cosh \frac{\pi\mu''}{\omega_1} + q^{4n}}\right)$$

Also, the substitution of equation [47] into equation [33] yields

$$-\alpha + i\beta = \frac{\gamma}{\pi}\left[-\frac{i}{\omega_3}\pi\nu - i\frac{i}{\omega_3}\frac{\pi\nu\mu''}{\omega_1}\right.$$
$$+ i \cdot 2 \tan^{-1}\left(\tan \frac{\pi\nu}{2\omega_1} \cdot \tanh \frac{\pi\mu''}{2\omega_1}\right) \qquad [48]$$
$$\left. + i \cdot 2 \sum_{n=1}^{\infty} \tan^{-1}\left(\frac{2q^{2n} \sin \frac{\pi\nu}{\omega_1} \cdot \sinh \frac{\pi\mu''}{\omega_1}}{1 + 2q^{2n} \cos \frac{\pi\nu}{\omega_1} \cdot \cosh \frac{\pi\mu''}{\omega_1} + q^{4n}}\right)\right]$$

From the imaginary part of equation [48] the following result is obtained:

$$\frac{\beta}{\alpha} = -\frac{\mu''}{\omega_1} + \frac{\gamma}{\alpha}\frac{2}{\pi}\left[\tan^{-1}\left(\tan \frac{\pi\nu}{2\omega_1} \cdot \tanh \frac{\pi\mu''}{2\omega_1}\right)\right.$$
$$\left. + \sum_{n=1}^{\infty} \tan^{-1}\left(\frac{2q^{2n} \sin \frac{\pi\nu}{\omega_1} \sinh \frac{\pi\mu''}{\omega_1}}{1 + 2q^{2n} \cos \frac{\pi\nu}{\omega_1} \cdot \cosh \frac{\pi\mu''}{\omega_1} + q^{4n}}\right)\right] \qquad [49]$$

On the other hand, at the surface of the electrode, it is clear that $s = \omega_1 + is''$ and $x = \alpha$. Substituting these coordinates into equation [31], one obtains

$$\frac{\gamma}{\alpha} = -\frac{s''}{\omega_1} + \frac{\gamma}{\alpha}\frac{2}{\pi}\left[\tan^{-1}\left(\tan \frac{\pi\nu}{2\omega_1} \cdot \tanh \frac{\pi s''}{2\omega_1}\right)\right.$$
$$\left. + \sum_{n=1}^{\infty} \tan^{-1}\left(\frac{2q^{2n} \sin \frac{\pi\nu}{\omega_1} \cdot \sinh \frac{\pi s''}{\omega_1}}{1 + 2q^{2n} \cos \frac{\pi\nu}{\omega_1} \cdot \cosh \frac{\pi s''}{\omega_1} + q^{4n}}\right)\right] \qquad [50]$$

Intensity of the Electric Field at the Electrode Surface

If the conjugate complex is denoted by $\bar{\mathfrak{R}}$, the intensity of the electric field $\mathfrak{E}_s$ can be represented as

$$\mathfrak{E}_s = \bar{\mathfrak{R}}\left[i\frac{ds}{dz}\right]_s \qquad [51]$$

where the suffix s means the electrode surface. Equations [3] and [30] yield

$$\frac{ds}{dz} = \frac{\pi}{\gamma}\frac{\wp(\nu) - \wp(\mu)}{\wp'(\nu)}\frac{\wp(s) - \wp(\nu)}{\wp(s) - \wp(\mu)} \qquad [52]$$

where $(ds/dz)_s$ proves to be a real number, because both $\wp(i\mu'' + \omega_1)$ and $\wp(is'' + \omega_1)$ are necessarily real when both $i\mu''$ and is'' are imaginaries, as is known from the nature of the $\wp$-function. Therefore:

$$\mathfrak{E}_s = -i\frac{\pi}{\gamma}\frac{\wp(\nu) - \wp(\mu)}{\wp'(\nu)}\frac{\wp(s) - \wp(\nu)}{\wp(s) - \wp(\mu)} \qquad [53]$$

Furthermore, this may be expressed in terms of the ϑ-function for the convenience of numerical calculation:

$$\mathfrak{E}_s = i\frac{\omega_1}{\gamma}\frac{1}{\frac{\alpha}{\gamma} + \frac{1}{\pi}\frac{\vartheta_1'(\nu_1)}{\vartheta_1(\nu_1)}\left[\frac{1}{i}\frac{\vartheta_1(is_1'')}{\vartheta_2(is_1'')}\right]^2 - \left[\frac{1}{i}\frac{\vartheta_1(i\mu_1'')}{\vartheta_2(i\mu_1'')}\right]^2} \qquad [54]$$

in which equations [17], [34], and [36] are taken together into account.

Fig. 3 to 7 show some examples of a tentative numerical calculation of the electrical field intensity on the electrode surfaces in an electrolytic cell whose width (2γ) is equal to the distance between the electrodes (2α). Although it is easily understood that the larger the electrodes and the nearer they are to the walls, the more uniform the electrical field intensity and the current distribution, this is shown in concrete and quantitative form in the figures. The per cent of current allotted to the inner and the outer surface of the electrode is given; total current in per cent is referred to over-all current when the electrodes touch the side walls, i.e., when $\beta = \gamma$.

The calculations shown in Fig. 3–7 were made for the

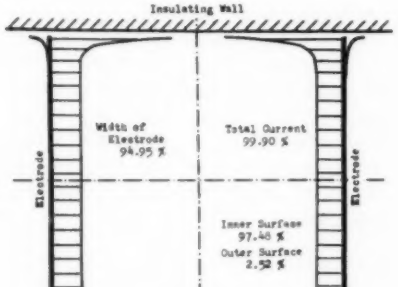

Fig. 3. Current distribution when the electrode width is 94.95% of the bath width.

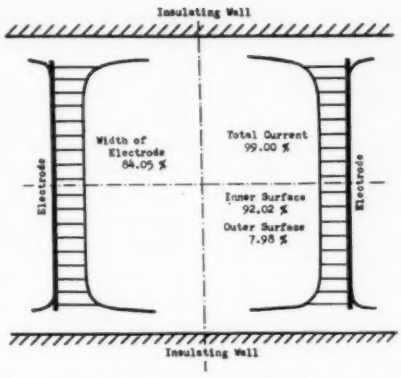

FIG. 4. Current distribution when the electrode width is 84.05% of the bath width.

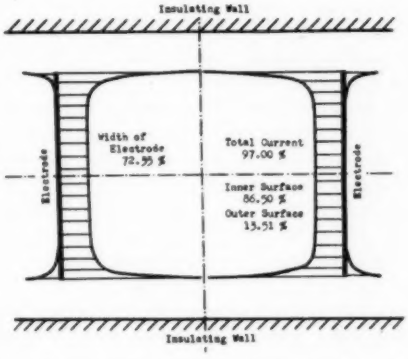

FIG. 5. Current distribution when the electrode width is 72.35% of the bath width.

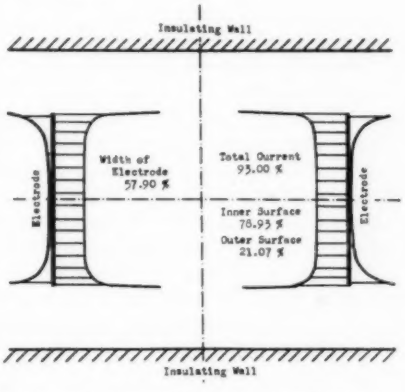

FIG. 6. Current distribution when the electrode width is 57.90% of the bath width.

special case where $\gamma/\alpha = 1$. Each new cell design requires an independent set of calculations, which are laborious and time-consuming. For this reason Fig. 8 has been prepared, as a more or less satisfactory approximation for practical use. The meaning and use of this figure are discussed below.

Diagram of Current Distribution in the Electrolytic Cell

On the abscissa of Fig. 8 is scaled, from left to right, the percentage of the width of the electrode to that of the cell ($\beta/\gamma \times 100\%$), so that the scale from right to left shows

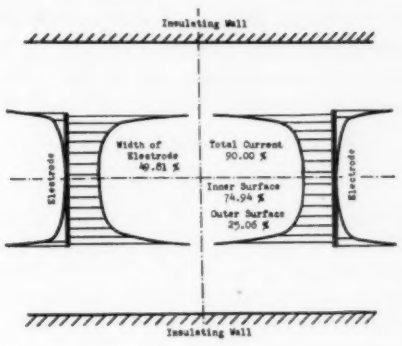

FIG. 7. Current distribution when the electrode width is 49.81% of the bath width.

the percentage of the gap between the edge of the electrode and the insulating wall [$(\gamma - \beta)/\gamma \times 100\%$]. The ordinate indicates the percentage of the electric current at the inner surface to the total current when read upward and that at the outer surface when read downward. The inner surface must carry 100% of the current when the electrode is as wide as the cell; the shares of both surfaces are equal in the extreme case of a point electrode. The current distribution is shown by the S-shaped lines, each of which represents a constant value of γ/α as labelled, from 1 to 100.

The finer lines numbered from 10 to 90 are the lines of equipercentage of the total current referred to the current when the electrodes touch the side walls. This percentage shows a characteristic decrement as the gap between electrode and wall grows larger.

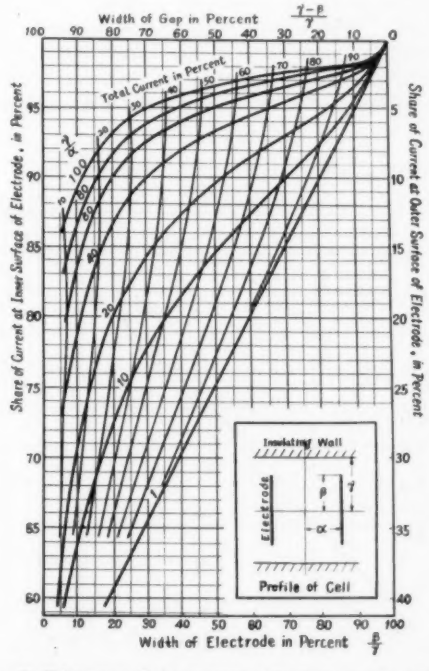
Width of Gap in Percent (γ−β)/γ
Total Current in Percent
Share of Current at Inner Surface of Electrode, in Percent
Share of Current at Outer Surface of Electrode, in Percent
Width of Electrode in Percent β/γ
Insulating Wall
Electrode
Profile of Cell

FIG. 8. Diagram of the current distribution at the suface of the electrode.

Explanation of Usage by a Numerical Example

The use of Fig. 8 can be clarified by consideration of a practical example. Assume electrodes 40 cm in width, 2 cm apart, immersed in a cell 50 cm wide. Then

$$\beta/\gamma \times 100 = (40/50) \times 100 = 80\%$$

$$\gamma/\alpha = 50/2 = 25$$

Although the diagram lacks a line at $\gamma/\alpha = 25$, one estimates the values: share of the inner surface, 95.5%; share of the outer surface, 4.5%. The current is about 85% of its value for the widest electrodes, since the point located above lies between the finer lines for 80% and 90%.

Discussion

In the analysis of the electric field shown in Fig. 2, the Weierstrass $\wp$-function was used for the Schwarz-Christoffel transformation. It is also possible to use Jacobi's function to arrive at the same conclusion, as Kiyono actually has done to confirm this method.

Although this investigation was confined to the effect of the side walls as stated earlier, similar analysis is possible in cases when side walls are sufficiently distant and back walls approach the electrodes. Such cases, however, are of small importance to industrial electrolytic cells.

As shown in Fig. 3 to 7, one may conclude that when cells of the same size and form are in question, larger electrodes cause better uniformity in the current distribution at the electrode surface, as far as the inner surface is concerned. This is not inconsistent with what experience has taught, but present results make the conclusion exact and concrete.

Electrodes which fit closely in the cell would seem at first glance to be ideal, since the current distribution is best, total current is highest for a given applied voltage, and power efficiency is greatest. But in actual practice technical difficulties arise, such as insufficient agitation of solution around the electrodes. When gases are evolved and must be expelled rapidly, as in the horizontal mercury cathode chlorine cell, it is advisable to have wider gaps than otherwise necessary, between electrodes and cell walls. Such dilemmas are often encountered, and other viewpoints are necessary to find the most economical cell design.

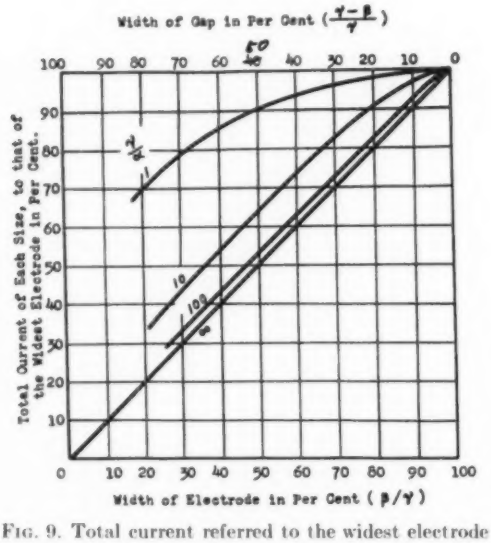
Width of Gap in Per Cent ($\frac{\gamma-\beta}{\gamma}$)
100 90 80 70 60 50 40 30 20 10 0
Total Current of Each Size, to that of the Widest Electrode in Per Cent.
90 80 70 60 50 40 30 20 10
$\frac{\gamma}{\alpha}$
1
10
100
∞
0 10 20 30 40 50 60 70 80 90 100
Width of Electrode in Per Cent (β/γ)

Fig. 9. Total current referred to the widest electrode

In combination with this question, the S-curves in Fig. 8 may be considered. The ratio γ/α becomes nearly 100 in an electrolyzer 40 to 50 cm wide with the electrodes as close to each other as 0.5 cm, as is exemplified in the horizontal mercury cathode chlorine electrolyzer. This type of horizontal cell requires special consideration, since the mercury cathode covers the entire cell profile, and β and γ may be nearly equal. In this case, neither the total current nor the distribution at inner and outer anode surfaces change much for the ratios of γ/α between 50 and 100, as seen in Fig. 8. If β/γ becomes smaller than 95%, however, the ratio γ/α has more importance. Ordinary cells for redox and oxidation electrolysis have γ/α equal to 10 to 30, and there are scarcely any industrial cells with γ/α as low as 1. Examples might be found in cells for electroplating, but these will not be discussed here, because the shapes of the cathodes are variable and accessory anodes are often used, making the geometric form of the cell quite different from the present model. It is not rare in laboratories to encounter a case where γ/α is 0.1, as in the Haring cell used to test throwing power in electroplating, or when electrodes are simply inserted in a beaker. Although such a case is not shown in Fig. 8, it is almost identical with the line for $\gamma/\alpha = 1$.

Examination of the curves in Fig. 8 for high values of γ/α shows that, after a small abrupt access of current to the outer electrode surface as the gap between wall and electrode is opened, the distribution changes only a few per cent until the gap width becomes very large. In this case, when the gap width is small, most of the current to the outer surface is concentrated at the edges.

On the other hand the larger the value of γ/α, the more rapidly the total current (at constant applied voltage) diminishes with decreasing electrode area (relative to cell width). This is illustrated more clearly in Fig. 9, where the ordinates represent total current, relative to maximum current with no gap. When $\gamma/\alpha = \infty$, indicating an infinitely wide electric field, the total current is simply proportional to electrode area. This is nearly true where $\gamma/\alpha = 100$; but when $\gamma/\alpha = 1$, the total current remains near its maximum value while the electrode area is reduced as much as 50%. This factor should not be overlooked in cell design, especially for large cells.

Summary

The electric field in an electrolytic cell has been analyzed as a function of electrode width and distance between electrodes, both relative to cell width, by the method of conformal transformation. The results obtained have been illustrated with various examples. The current distribution between inner and outer electrode surfaces, and the total current at constant applied voltage, as a function of relative electrode size, have been plotted in a comprehensive diagram as an aid in the design of new cells. For mathematical simplicity, the effects of the back walls and of electrode polarization have been neglected, but it is believed

that this will not detract from the usefulness of the diagram for industrial cell design.

Acknowledgments

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1956 Journal.

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Technical Review

Electrochemical Techniques in the Thermodynamics of Metallic Systems

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ABSTRACT

The use of galvanic cells employing nonaqueous electrolytes and operating at elevated temperatures is a relatively little known technique. Some of the details for the successful operation of such cells are described both for liquid and for solid alloys. The kind and the accuracy of the information obtained are discussed. Applications to the determination of phase diagrams are outlined, and the possibilities of obtaining surface free energies are discussed. A comprehensive bibliography of galvanic cell studies of metallic systems is presented.

Introduction

This paper is concerned only with the electrochemical techniques of use in studying the thermodynamics of metallurgical systems. In practice, the only such technique is that of the galvanic cell, which can be used to study both thermodynamic magnitudes and phase relationships. The first section of the paper is devoted to a brief account of the basic relations. The second section discusses the experimental procedures in some detail, and a subsequent section presents some examples of experimental results. The physical significance of these results is beyond the scope of this paper.

General Relations

The type of galvanic cell useful in alloy studies can be symbolized by

$$A(\mathrm{l,\ s})|\ A^{z+},\ \text{ionic electrolyte}\ |A_xB_y(\mathrm{l,\ s})$$

The more electropositive metal, A, and the metallic solution of that metal, may be in the solid or in the liquid state, but the physical set-up of the cell will be different for the different possibilities. At each electrode there is an equilibrium between the A^{z+} in the ionic electrolyte and the metallic state of A, so that the open-circuit emf reflects the difference in activity of species A in the two electrodes. Since one gram atom of metal A is transferred from pure A electrode to the alloy electrode by a current of $z\mathbf{F}$ coulombs ($\mathbf{F}$ = the Faraday equivalent = 23,066 cal/volt), the amount of work required is

$$-z\mathbf{F}E = \overline{\Delta G_A} \equiv \overline{G} - G_A^\circ \qquad \text{(I)}$$

where E is the emf, $\overline{G}$ is the partial molar Gibbs free energy of A in the metallic solution, and G_A° is the molar Gibbs free energy of pure A in the state of aggregation of the electrode A. If one selects pure A at the existing state of aggregation of the A-electrode at temperature T as the reference state, equation (I) becomes (R = gas constant = 1.987 cal/deg. g-atom)

$$-z\mathbf{F}E = RT \ln a_A - RT \ln 1 = RT \ln a_A \qquad \text{(II)}$$

It is generally preferable to use as reference state the pure metal of the same state of aggregation as that of the metallic solution at the temperature in question. A change of reference state with respect to state of aggregation may readily be made by remembering that the free energy difference between pure liquid and pure solid is given by

$$G_{\mathrm{liq}}^\circ - G_{\mathrm{sol}}^\circ = \Delta S^0(T_0 - T) \qquad \text{(III)}$$

in which ΔS^0 is the entropy of fusion of the pure reference substance, assumed independent of the temperature, and T_0 is the melting temperature of the pure reference substance. For example, suppose that the measured E is that developed by a solid solution against a pure liquid electrode. Then, the activity calculated by (II), $\ln a_A' = -z\mathbf{F}E/(RT)$, will refer the activity of A in the solid solution to the pure liquid A. In order to refer the activity to pure solid, the following scheme is useful:

$$\text{Add}\quad \begin{cases} A_{(l)} = A(B)_{(s)},\ \overline{\Delta G_A}' = RT \ln a_A' \\ A_{(s)} = A_{(l)},\ \Delta S_A^0(T_0 - T) \end{cases}$$

$$A_{(s)} = A(B)_{(s)},\ \overline{\Delta G} + \Delta S_A^0(T_0 - T)$$

$$= \overline{\Delta G_A} = RT \ln a_A$$

Measuring the emf as a function of temperature, as long as each electrode is single-phased, yields the partial molar entropy of solution, $\overline{\Delta S_A}$, since $(\partial E/\partial T)_x = (\partial/\partial T)\ (-\overline{\Delta G_A}/z\mathbf{F}) = \overline{\Delta S_A}/(z\mathbf{F})$. The reference state for this quantity is again the state of aggregation of the pure electrode actually employed, and changes in reference state may be carried out by a scheme analogous to that given above for the free energy. The partial molar enthalpy of solution, $\overline{\Delta H}_A$, may be calculated from the relation $\overline{\Delta G_A} = \overline{\Delta H}_A - T\overline{\Delta S_A}$, and the same remarks apply to this quantity.

After measurements of the partial molar properties of component A have been carried out as a function of concentration, the partial molar properties of the second constituent in the binary system may be obtained by

graphical integrations of the Gibbs-Duhem equation. The most convenient form for graphical integration is

$$\overline{\Delta A_B}^E(x) = \int_0^X \frac{\overline{\Delta A_A}^E}{(1-x)^2}\,dx - \frac{\overline{x\Delta A_A}^E}{1-x} \qquad \text{(IV)}$$

where $\overline{\Delta A_i}^E$ represents the excess partial molar property (the free energy, entropy, or enthalpy) of component i, and x is the mole fraction of component A. The excess partial molar property is defined relative to the value of that property for an ideal solution, i.e.,

$$\overline{\Delta A_i}^E = \overline{\Delta A_i} - \overline{\Delta A_i}\ \text{(ideal)} \qquad \text{(V)}$$

The excess integral molar properties may be formed by combining the excess partial molar properties of the two components:

$$\Delta A^E = \overline{x\Delta A_A}^E + \overline{y\Delta A_B}^E \qquad \text{(VI)}$$

Darken (1) and Wagner (2) have presented computational methods for ternary systems.

Experimental Details

General Considerations (3)

Implicitly behind the above calculations is the assumption that the galvanic cell has behaved reversibly in order that the data be thermodynamically meaningful. From an empirical point of view, the criteria of reversibility are the time-independence of an emf at constant temperature, the reproducibility of a value of emf irrespective of whether it is approached from the high temperature or from the low temperature side, and recoverability of a value of emf after passage of a small amount of current through the galvanic cell in either direction. In order to achieve reversibility, the experimental conditions must be adjusted in the light of the following considerations. First, the electrolyte must exhibit only ionic conductivity, and the valence of the ion of the more electropositive metal as it exists in the electrolyte must be definite and known. These conditions follow from the necessity that the partial molar free energy be described by equation (I).

Second, only one reaction should occur at the electrode interface: $A \rightleftharpoons A^{z+} + ze$. This implies that oxidizing and reducing agents must be avoided in the electrolyte, in the gaseous atmosphere above the electrolyte, and in the vessel material. It also means that the extent of the analogous reaction, $B \rightleftharpoons B^{p+} + pe$, for the less electropositive component must be negligible. One can estimate the extent of this reaction by calculating the free energy of the reaction

$$zB + pACl_z \rightleftharpoons zBCl_p + pA \qquad \text{(VII)}$$

if, for example, chloride is the anion of the electrolyte. If the equilibrium point for the above reaction is not sufficiently far toward the left, it may be possible that changing to some other anion would increase the disparity between the metals A and B.

Third, it is necessary that the temperature of operation be high enough to enable diffusion to equalize activity gradients between the interior and the surface of the electrode. Such gradients will come about because of the finite value of the equilibrium constant of reaction (VII), and because small flows of current such as inevitably accompany the balancing of the potentiometer circuit used for measurement of the emf will change the concentration of electropositive metal at the electrode-electrolyte interface. Experience has shown that operating temperatures not lower than 0.3 or 0.4 of the absolute melting temperature of the alloy are suitable.

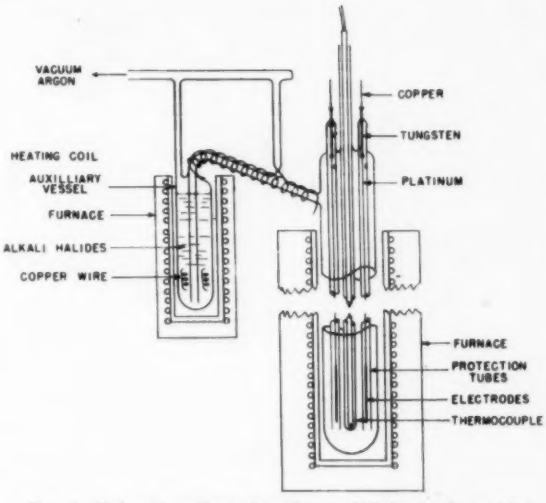

Fig. 1. Galvanic cell employed for solid electrodes at high temperatures.

In addition to considering the reversibility of the cell, attention must be paid to minimizing the thermoelectric emf developed by the cell, which adds algebraically to the purely galvanic emf. The furnace gradient should be as small as possible, and the thermoelectric effect should be measured in separate experiments in which all experimental conditions of the main experiment are reproduced except that the electrolyte is omitted, and the alloy and reference electrodes are interconnected within the cell.

Constructional Details (4)

The construction of a galvanic cell that has been found useful for the study of solid alloys with a solid reference electrode is shown in Fig. 1. The electrodes are spot-welded to the lead wires made of tungsten or of platinum; the lead wires are spot-welded to tungsten-Pyrex seals at the top, and connection to the potentiometer circuit is made by copper clips. This cell is designed to be used up to about 1100°C with mixtures of alkali metal chlorides as the electrolyte. Silica is an excellent construction material for use with fused chlorides as long as the latter are free of water. The cell shown in Fig. 1 has silica tubes surrounding each electrode in order to avoid accidental contact among the electrodes, and in order to reduce diffusive and convective transport of material through the electrolyte. This latter purpose is important because the finite magnitude of the equilibrium constant for the reaction

$$zB + pA^{z+} \rightleftharpoons zB^{p+} + pA \qquad \text{(VIII)}$$

furnishes a mechanism for the transport of metal from one electrode to another, with a consequent change in composition.

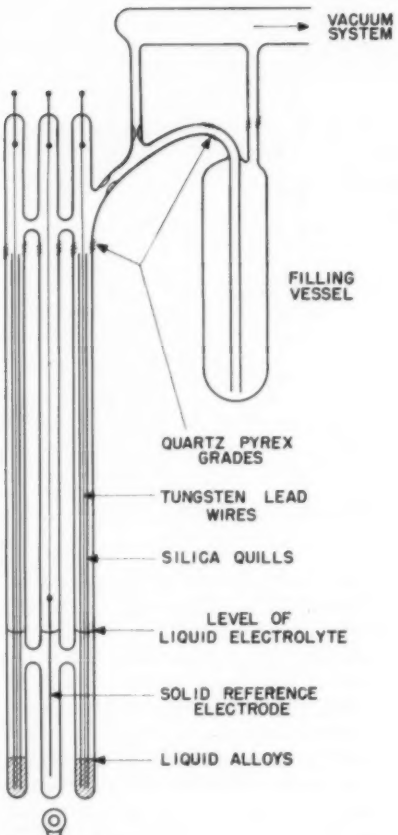

FIG. 2. Galvanic cell employed for liquid alloys and solid reference electrode at high temperatures.

Other electrolytes may be found useful as long as they are ionic conductors, have rather low vapor pressures, are stable at the temperatures involved, and a construction material can be found that is inert toward them. These requirements restrict the possibilities markedly. Hauffe and Vierk (5), Vierk (6), Kubaschewski and Huchler (7), Frauenschill and Halla (8), and Croatto and Bruno (9) have employed solid glasses as electrolytes. Molten metaborates may be used. Vatolin and Esin (10) have used a molten mixture of oxides and sodium sulfide, and Sanbongi and Ohtani (11) employed a "carbide slag" dissolved in high melting oxides for the measurements of the activity of sulfur and of carbon, respectively, in molten iron. Sometimes the charge carried by the relevant ion in the electrolyte may be in doubt and accessory experiments may be necessary to determine it. The ceramic known as Mullite is a useful construction material for holding some liquid oxides; its utility is enhanced by the fact that it can be joined to Nonex glass. The electrolyte most commonly used in high temperature galvanic cells is the eutectic mixture of KCl and LiCl, which melts at 360°C. Lower melting temperatures may be obtained by adding RbCl to the eutectic mixture.

Fig. 2 shows a cell designed for use at about 1100°C for the combination of liquid alloys and solid reference electrode. The tungsten or platinum lead wires are enclosed in thin-walled silica quills which are kept in position by being spotted near their upper ends to the silica vessel. This cell design provides a long diffusion path between electrodes through the electrolyte.

Operational Details

Once the galvanic cell has been constructed and well-homogenized alloys of known composition have been sealed in place, there remains the pretreatment of the electrolyte and of the cell. The objective of the pretreatment is to rid the electrolyte and cell walls of all deleterious material, generally moisture, oxidizing agents, and material decomposable at the temperatures of cell operation. The method to be used depends on the nature of the electrolyte. The procedure used by the writer for the KCl-LiCl mixture is described as illustrative of the necessary precautions.

The salt mixture is introduced into a filling vessel, such as shown in Fig. 2. An amount of the lower chloride of the more electropositive metal is added; in general, the amount of ACl_z to be added should be quite small, 0.5% or less, in order to restrain the formation of B^{p+} ions according to equation (VIII). However, there is indication in the literature that in some cases, too small an amount of ACl_z will lead to irreversible behavior of the cell, so that the optimum amount must be determined by trial. In the filling vessel is placed a clean strip or wire of the pure metal B which serves to reduce any higher chlorides of B that may be present.

After the filling vessel and cell are interconnected and attached to a vacuum system, both the filling vessel and cell are heated under vacuum in separately controlled furnaces. The salt mixture is maintained liquid at 500°C for about one week in order to destroy any chlorates present, and to desiccate the salts thoroughly. The cell is maintained at as high a temperature consistent with the vapor pressure of the metals involved in order to desiccate the walls of the cell thoroughly. After this treatment, the electrolyte is transferred to the cell by first sealing off the vertical connecting tube between cell and vacuum system, then admitting pure helium over the liquid in the filling vessel to force the liquid up and over into the cell. The auxiliary heating coil shown in Fig. 1 is not necessary if gas flames are used to preheat the connecting tube. After all the electrolyte has been transferred, more helium is admitted until the pressure is about half an atmosphere, whereupon the cell is sealed off. The helium serves to repress volatilization of the fused salts. Using this method of preparation, the writer has been able to operate a galvanic cell for nine months after which the silica did not show any attack at all. Unfortunately, this electrolyte wets silica so well that if the salts are allowed to freeze the cell invariably breaks.

After filling the cell, it is usually found necessary to wait from some hours to days before the electrode emf's become stable at constant temperature. The reason for this aging period is not clear, though it may be associated with the establishment of the equilibrium (VIII). Since

this equilibrium cannot be satisfied simultaneously for various electrodes of different compositions, it seems best to use electrodes of similar compositions when data of highest accuracy are required. After the electrode emf's become stable, data can be taken at a speed that depends on the furnace constant, whether the alloys are liquid or solid, and whether or not the alloys are undergoing a metallurgical transformation. With liquid alloys, data points can be obtained as rapidly as the furnace permits a change of temperature. With solid alloys, the waiting times at constant temperature should be such that no further changes are observed, the magnitude of the permissible change in the emf being regulated by the accuracy desired. In any case, reproducibility of measurements taken with decreasing and with increasing temperatures is the final criterion of the adequacy of the procedure. Any one emf reading should be done by a potentiometer the key of which should be depressed only momentarily since the galvanic cell is easily polarized.

Experimental Information

The primary result of galvanic cell investigations of the type here described is information relating to the thermodynamics of solutions. This includes numbers for the thermodynamic activities of the constituents and, therefore, the free energy of solution, i.e., of formation, the partial and integral enthalpies of solution, and the partial and integral entropies of solution. In principle, it is also possible to measure the deviation of the heat capacity of the alloy from the Kopp-Neumann rule of additivity by measuring the variation of the enthalpy of solution with temperature, but in practice the accuracy of the measurements is almost never great enough. Useful tabulations of results of galvanic cell studies are given by Wagner (3), Kubaschewski and Evans (4), and by Chipman and Elliott (12) for liquid alloys.

It is difficult to assess the accuracy of emf studies. The limiting factor is certainly not the accuracy with which a voltage may be measured, but usually is associated with the extent to which ions of the more noble metal are produced. Less subtle are the errors associated with temperature measurement, chemical analysis of the alloys, and failure to correct for thermoelectric effects. It sometimes happens also that investigators fail to wait long enough for metallurgical changes, such as changes of phase, or of degree of order, so that equilibrium is not achieved in the time allotted.

Measurement of entropies of solution, depending as they do on the temperature variation of an emf, may have a relative error of five to ten times that in the value of the free energy itself. The computation of the partial molar property of component B from the measured values of A also introduces error, not only because of the errors inherent in a graphical integration, but also because of the necessary extrapolation to $x = 0$ of the integrand. It is in this connection that the use of excess partial molar quantities in equation (IV) is advantageous, because then the integrand extrapolates to a finite value as $x \to 0$ rather than to negative infinity as occurs when partial molar $\overline{\Delta G_A}$ and $\overline{\Delta S_A}$ are used. The calculation of the enthalpy from the free energy and the product of temperature and entropy depends on the difference of two numbers, so that the errors of each accumulate in the difference. Therefore, it is very worth while to carry out independent calorimetric determinations of the enthalpy of solution.

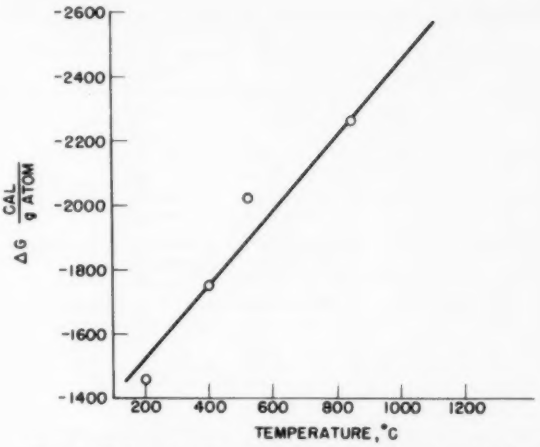

Fig. 3. Galvanic cell results for the integral molar free energy of formation of solid $Ag_{1/2}Au_{1/2}$: 200°C, solid AgCl as electrolyte (17); 400°C, solid glass as electrolyte (7); 527°C, liquid KCl + AgCl as electrolyte (16); 850°C, liquid KCl + LiCl + AgCl as electrolyte (18).

Empirically, there are two ways of estimating the accuracy of galvanic cell measurements of thermodynamic properties. The first is to compare the results of galvanic cell work of various investigators of the same alloy system, particularly when different electrolytes are used. The second way is to compare galvanic cell results with those from other techniques. As an example of the use of different electrolytes, although by the same investigators (13), there are the galvanic cell studies on liquid Pb-Bi solutions using both LiCl-KCl and sodium acetate as electrolytes, between which excellent agreement exists. The liquid Cd-Sb system has been investigated by the emf technique both by Seltz and DeWitt (14), and by Chipman and Elliott (15), again with excellent agreement. Fig. 3 shows the results of four galvanic cell investigations (7, 16–18), at different temperatures and with four types of electrolytes, of solid Ag-Au alloys. Table I presents the enthalpy of formation derived from the same measurements; the agreement among the ΔH values is not so good as that shown by the ΔG-T results. Table II shows the excellent agreement obtained by two galvanic cell investigations (19, 20) using the same electrolyte with solid, disordered $Au_{1/2}Cu_{1/2}$ both for the ΔH and the ΔS of solution. These examples are merely illustrative, and certainly do not exhaust the available cases where good agreement exists among various galvanic cell studies.

A comparison of the results of galvanic cell studies with those of other thermodynamic techniques is more pertinent. Hildebrand and Eastman's (21) vapor pressure measurements on thallium amalgams agree within a few per cent with the emf measurements of Richards and Daniels (22). Schmahl's (23) measurements of the activity of Ag in solid Ag-Au alloys at 550° by a chemical equilibration technique agree very well with the galvanic

TABLE I. *Heat of formation of solid* $Ag_{1/2}Au_{1/2}$ *from galvanic cell studies*

ΔH, cal/gram atom	Reference
−1300	(16)
−947	(17)
−950	(7)
−970	(18)

TABLE II. *Heat and entropy of formation of disordered* $Au_{1/2}Cu_{1/2}$ *from galvanic cell studies*

ΔH, cal/gram atom	ΔS, cal/deg.-g.atom	Reference
−1230	1.26	(19)
−1200	1.31	(20)

cell results at 525°C of Wagner and Engelhardt (24). Gonser's (25) determination of the activities in liquid Pb-Bi alloys agree very well with the emf results of Strickler and Seltz (13). The ΔH of solution of solid $Cu_{3/4}Au_{1/4}$ from emf measurements (20) was found to be −1080 cal/gram atom at 427°C, which compares favorably with the calorimetrically determined value (26) of −1124 ± 55 cal/gram atom at 0°C. Similarly, the emf value (18) for the ΔH of solution for solid $Ag_{0.42}Au_{0.58}$ is −940 cal/gram atom at 850°, to be compared with a calorimetric value (27) of −1010 ± 25 cal/gram atom at 0°C.

The galvanic cell can be used to yield information not only on the thermodynamic properties of the solution referred to its constituents, but also on the phase relations within the alloy system. Such information is obtained from the principle that across a two-phase region an isothermal line is also an isoactivity line; it is implied that the identical reference state is used for any one component in all the phases concerned. Dunkerley and Mills (28) give a valuable review of the use of emf data in establishing phase boundaries; in this connection the monograph by Lumsden (29) should also be consulted. There is space here to refer only to a case where the galvanic cell technique proved particularly apt in establishing phase boundaries (20). Fig. 4 shows the phase relationships about the superlattices in CuAu. The solid points were obtained directly from the temperatures at which the emf-temperature curves showed inflections; the open points were obtained from the measurements of activity and the condition of isoactivity across a two-phase field. The results show that the superlattices in this system are Gibbsian phases, a question which has been the topic for much debate.

Applications to Interfaces

The galvanic cells under consideration in this paper depend for their success, among other factors, on diffusive interchange between the interior of the electrode and the electrode-electrolyte interface. A galvanic cell, $Cu|Cu^{++}$ aq | calomel electrode, operating at room temperature can respond only to the atoms of copper directly in contact with the aqueous electrolyte. Tragert and Robertson (30) used such a cell, and, by amalgamating the surface of single crystals of copper to provide a mechanism for surface mobility, have been able to show qualitatively that the oxidation potential of the copper is dependent on the crystallographic configuration of the atoms on the surface, and that the (111) plane has the lowest oxidation potential, and hence presumably the lowest activity.

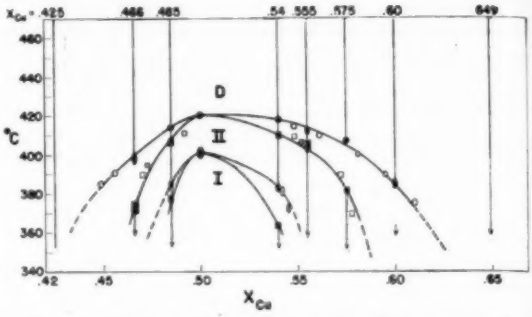

FIG. 4. Phase relationships about the composition $Cu_{1/2}Au_{1/2}$ as established by the galvanic cell technique. *D* represents the f.c.c. disordered solid solution, II represents the orthorhombic superlattice, and I the tetragonal superlattice.

However, a galvanic cell may in principle be used to obtain quantitative, equilibrium information on interfacial free energy. The following experiment is proposed as a method for obtaining the surface tension of a solid and its temperature variation, that is, the surface entropy. Set up the cell, $Ag_{(s)}|\ Ag^+,\ KCl,\ LiCl\ |Ag_{(s)}$, where silver is used as an example. One electrode is a pure silver bar of normal diameter, 1/16 in. or larger; the other electrode is a very fine wire of uniform diameter, say 0.0005 in., of the same silver. The emf between these electrodes, after correction for any thermoelectric emf, will depend on the diameter, d, of the narrow wire and the interfacial free energy of silver, σ, according to the relation

$$E = -\frac{2\sigma V_m}{z\mathbf{F}d} \qquad \text{(IX)}$$

where V_m is the molar volume of the metal. Using 1000 ergs/cm² as an estimate for the interfacial energy of silver, the observed emf would be about 20 μv, a magnitude within experimental accessibility. This experiment would yield the interfacial free energy of the metal-fused salt interface, a quantity of lesser immediate theoretical significance than the interfacial free energy of the metal-vacuum interface.

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1956 JOURNAL.

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Bibliography of Galvanic Cell Studies of Metallic Systems

The numbers in brackets following the temperature range and the composition range indicate the number of temperatures and of compositions studied in the cases where it is convenient so to indicate. The state of aggregation of the alloy electrodes is signified in the fourth column by S for solid and L for liquid. This compilation is intended to be as comprehensive as possible up to June 1955, and is based on a preliminary list prepared by Leslie Seigle and David Turnbull, General Electric Research Laboratory Report 108. The aid of W. K. Murphy in checking the references is gratefully acknowledged.

System	Temp. range, °C	Comp. range, mole % of 1	State	Reference
1 2				
Ag-Al	370–550 [3]	5–95 [14]	S	(1)
Ag-Au	1085	26–85 [5]	L	(2)
	1030–1140	11–73 [11]	L	(3)
	413–774	8–80 [7]	S	(2)
	850	11–73 [8]	S	(3)
	200–430	15–86 [7]	S	(4)
	720–890	25–94	S	(5)
	300–630	4–73	S	(6)
Ag-Cd	410–450 [5]	0.5–5.2 [6]	L	(7)
	400–500 [2]	20–60	S	(8)
Ag-Cd-Hg	16	[11]	L	(61)
Ag-Hg-Pb	17	[9]	L	(61)
Ag-Hg-Zn	16	[8]	L	(61)
Ag-Sb	430–470 [2]	68–98	S	(9)
Ag-Sn	627	0–70 [9]	L	(10)
	333–412 [5]	0.6–14 [10]	L	(11)
Au-Bi	600–800 [3]	5–79 [22]	L	(12)
Au-Cd	250–730	2–84 [62]	S	(17)
Au-Cd-Hg	16	[8]	L	(61)
Au-Cu	390–605	14–93 [8]	S	(2)
	400–850 [6]	10–93 [9]	S	(13)
	345–490	23–57 [12]	S	(14)
	930–1040	15–85 [8]	L	(3)
	250–700	5–85 [22]	S	(15)
Au-Hg-Pb	17	[9]	L	(61)
Au-Hg-Zn	16	[13]	L	(61)
Au-Ni	700–900	5–95	S	(16)
Au-Pb	450–800	4–79 [18]	L	(18)
Au-Sb	315–355	50–75	S	(19)
Au-Sn	269–370 [3]	0.2–5.5 [10]	L	(11)
	500–600	25–90 [13]	L	(20)
Au-Tl	600–800 [3]	10–82 [17]	L	(12)
Ba-Hg	25	0.16×10^{-3}–3.8×10^{-3}	L	(60)
Bi-Cd	420–580 [4]	14–89 [16]	L	(21)
	400–600	5–90 [10]	L	(22)
	400–650	10–89	L	(33)
Bi-Cd-Pb	380–600	[11–94] Cd; Pb/Bi = 0.5–1.9	L	(23)
Bi-Cd-Sn	410–475 [5]	[5–90] Cd; [0–75] Sn [9]	L	(24)
Bi-Ce-Hg	18	[10]	L	(61)
Bi-Pb	124–213	5–33	S	(25)
	360–480 [7]	15–89 [8]	L	(25)
	475–665 [2]	28–92 [7]	L	(2)
Bi-Sn	330	23–92 [9]	L	(2)
	412–500 [6]	16–90 [9]	L	(26)
Bi-Tl	120–295	3–84	S	(27)
	270–480 [2]	17–80 [6]	L	(2),
	495	5.5–87.5 [8]	L	(62)
Bi-Zn	600	3–94 [19]	L	(28)
C-Fe	1440–1540	0.1–4.4 [13]	L	(29)
Cd-Cu	410–550 [5]	91.5–99.6 [7]	L	(7)
Cd-Cu-Hg	16	[8]	L	(61)
Cd-Hg	25–75 [3]	1–100 [32]	L	(30)
	25	10^{-6}–3.8 [9]	L	(61)
Cd-Hg-Na	300–400 [14]	[10–90] Na; [25–75] Cd	L	(58)
Cd-Mg	270–300	3–99.5	S	(31)
Cd-Na	395	10–85 [9]	L	(32)
Cd-Ni	410–556 [5]	94.4–99.5 [7]	L	(7)
Cd-Pb	427–572 [4]	12–79	L	(21)
	400–600	10–95 [10]	L	(22)
Cd-Pb-Sb	380–600	[8–95] Cd; Pb/Sb = 0.5–2	L	(23)
Cd-Pb-Sn	380–600	[11–95] Cd; Pb/Sn = 0.5–2	L	(23)

System	Temp. range, °C	Comp. range, mole % of 1	State	Reference
1 *2*				
Cd-Sb	240–290	26–86 [8]	S	(34)
	395–435	37–43 [3]	S	(35)
	400–600	14–95 [9]	L	(22)
Cd-Sn	400–600	10–95 [9]	L	(22)
	432–585 [4]	8–82 [8]	L	(21)
	430–550	[7]	L	(59)
Cd-Te	355–440	5–15 [4]	S	(36)
Cd-Zn	435–540 [3]	15–85 [12]	L	(21)
Ce-Hg-Sn	18	[10]	L	(61)
Co-Pt	700–900	32–73 [8]	S	(37)
Cu-Hg-Zn	16	[6]	L	(61)
Cu-Pt	400–650	14–98 [14]	S	(38)
Cu-Zn	333–626	5–58	S	(39)
Fe-S-C	1250	(0.05–33) S; C sat'd.	L	(40)
Fe-Si	1450–1540	0–99.9 [27]	L	(41)
Hg-K	0–50 [5]	98–99.98 [8]	L	(42)
Hg-Mg-Sn	18	[12]	L	(61)
Hg-Na	−40–320	15–95	S	(43)
	5–25 [3]	95–99.6 [7]	L	(44)
	21–45 [20]	20–45	L	(45)
	15–35 [3]	45–98 [17]	L	(46)
	299–375 [2]	10–61 [15]	L	(32)
Hg-Na-Pb	350–400	(10–90) Na; Hg/Pb = 1–4 [9]	L	(47)
Hg-Pb	17	[11]	L	(61)
	95–155	[1]	L	(63)
Hg-Tl	−74–−8	70–78	S	(48)
	20–40	57–99.7 [12]	L	(49)
Hg-Zn	12–50 [4]	0.6–93 [15]	L	(50)
	16	[13]	L	(61)
	18–30 [3]	[18]	L	(64)
In-Zn	362–517 [4]	10–100 [13]	L	(51)
Na-Pb	425–475 [2]	34–94 [14]	L	(65)
Na-Sn	480	27–95 [19]	L	(65)
Na-Tl	352–375 [2]	25–96 [18]	L	(65)
Pb-Sb	370–630	11–87 [9]	L	(52)
	450–750		L	(53)
Pb-Sn	410–550 [5]	1–9.2	L	(7)
Pb-Te	355–408	16–40	S	(36)
Pb-Tl	352–478	21–90 [16]	L	(54)
	245–295	4–84	S	(55)
Pb-Zn	653	1–96 [16]	L	(28)
Sb-Sn	333–412 [5]	0.6–14 [45]	L	(11)
	632	10–90 [9]	L	(56)
Sb-Zn	560–700	15–68 [16]	L	(57)
Sn-Te	270–395	5–15	S	(36)
Sn-Tl	414–478 [3]	10–79 [16]	L	(54)
	462	7.2–94.5 [7]	L	(62)
Sn-Zn	430–570 [4]	15–86 [12]	L	(21)
Te-Zn	355–418	86–96	S	(36)

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MANUSCRIPTS AND ABSTRACTS FOR FALL MEETING

Papers are now being solicited for the Fall Meeting of the Society, to be held at the Statler Hotel in Cleveland, September 30, October 1, 2, 3, and 4, 1956. Technical sessions will be scheduled on Batteries, Corrosion, Electrodeposition, Electrothermics and Metallurgy, and Theoretical Electrochemistry (joint symposium with Electrodeposition).

To be considered for this meeting, triplicate copies of abstracts (not to exceed 75 words in length) must be received at Society Headquarters, 216 West 102nd St., New York 25, N. Y., *not later than June 15, 1956. Please indicate on abstract for which Division's symposium the paper is to be scheduled.* Complete manuscripts should be sent in triplicate to the Managing Editor of the Journal at the same address.

***

The Spring 1957 Meeting will be held in Washington D. C., May 12, 13, 14, 15, and 16, at the Statler Hotel. Sessions will be announced in a later issue.

FUTURE MEETINGS OF
The Electrochemical Society

San Francisco, April 29, 30, May 1, 2, and 3, 1956

Headquarters at the Mark-Hopkins Hotel

Sessions will be scheduled on

Corrosion (joint symposium with Theoretical), Electric Insulation, Electronics (including Luminescence and Semiconductors), Electrothermics and Metallurgy, Industrial Electrolytics, and Theoretical Electrochemistry

* * *

Cleveland, September 30, October 1, 2, 3, and 4, 1956

Headquarters at the Statler Hotel

Sessions will be scheduled on

Batteries, Corrosion, Electrodeposition, Electrothermics and Metallurgy, and Theoretical Electrochemistry (joint with Electrodeposition)

* * *

Washington, D. C., May 12, 13, 14, 15, and 16, 1957

Headquarters at the Statler Hotel

* * *

Buffalo, October 6, 7, 8, 9, and 10, 1957

Headquarters at the Statler Hotel

* * *

New York, April 27, 28, 29, 30, and May 1, 1958

Headquarters at the Statler Hotel

* * *

Ottawa, September 28, 29, 30, October 1, and 2, 1958

Headquarters at the Chateau Laurier

* * *

Papers are now being solicited for the meeting to be held in Cleveland. Triplicate copies of each abstract (*not exceeding 75 words in length*) are due at the Secretary's office, 216 West 102nd Street, New York 25, N. Y., *not later than June 15, 1956* in order to be included in the program. *Please indicate on abstract for which Division's symposium the paper is to be scheduled.* Complete manuscripts should be sent in triplicate to the Managing Editor of the JOURNAL at the same address.

San Francisco Program

THE ELECTROCHEMICAL SOCIETY

One Hundred and Ninth Meeting

—o—

Sunday through Thursday

April 29, 30, May 1, 2, and 3, 1956

CONDENSED TECHNICAL PROGRAM

Corrosion — Theoretical Electrochemistry (Abstracts 1–14)

(All sessions in Bonanza Room, Mezzanine)

Monday morning, April 30—10:00 A.M.–12:15 P.M.

Monday afternoon, April 30—2:00 P.M.–5:00 P.M.

Tuesday morning, May 1—9:00 A.M.–12:00 M.

Electric Insulation (Abstracts 15–25)

Monday morning, April 30—10:00 A.M.–12:00 M.
(Argonaut Room, Mezzanine)

Monday afternoon, April 30—2:00 P.M.–5:00 P.M.
(Argonaut Room, Mezzanine)

Tuesday morning, May 1—9:30 A.M.–11:45 A.M.
(Argonaut Room, Mezzanine)

Tuesday afternoon, May 1—2:00 P.M.–5:00 P.M.—Paper and Round-Table Discussion
(Golden Empire and Bonanza Rooms, Mezzanine)

Electronics — Luminescence (Abstracts 26–45)

(All sessions in Argonaut Room, Mezzanine)

Wednesday morning, May 2—9:10 A.M.–12:00 M.

Wednesday afternoon, May 2—2:00 P.M.–4:30 P.M.

Thursday morning, May 3—9:00 A.M.–11:45 A.M.

Thursday afternoon, May 3—2:00 P.M.–3:00 P.M.

Electronics — Semiconductors (Abstracts 46–60)

(All sessions in Peacock Court, Lobby)

Wednesday morning, May 2—9:00 A.M.–12:00 M.

Wednesday afternoon, May 2—2:00 P.M.–5:00 P.M.

Thursday morning, May 3—9:00 A.M.–12:00 M.

Thursday afternoon, May 3—2:00 P.M.–5:00 P.M.

Electrothermics and Metallurgy—Arcs in Inert Atmospheres and Vacuum (Abstracts 61–75)

(All sessions in Room of the Dons, Lobby)

Monday morning, April 30—10:00 A.M.–12:00 M.

Monday afternoon, April 30—2:15 P.M.–4:15 P.M.

Tuesday morning, May 1—9:00 A.M.–11:00 A.M.

Tuesday afternoon, May 1—2:00 P.M.–4:00 P.M.

Electrothermics and Metallurgy—Marginal Ores (Abstracts 76–83)

(All sessions in Golden Empire Room, Mezzanine)

Monday morning, April 30—10:00 A.M.–12:00 M.

Monday afternoon, April 30—2:15 P.M.–4:15 P.M.

Electrothermics and Metallurgy—Pyrometallurgical Refining of Reactor Fuels (Abstracts 84–89)

Wednesday morning, May 2—9:00 A.M.–12:00 M.
(Golden Empire and Bonanza Rooms, Mezzanine)

Electrothermics and Metallurgy—Rare Earths (Abstracts 90–94)

Wednesday afternoon, May 2—2:00 P.M.–4:30 P.M.
(Bonanza Room, Mezzanine)

Electrothermics and Metallurgy—Recent Developments in Superrefractories (Abstracts 95–106)

Wednesday afternoon, May 2—2:00 P.M.–4:00 P.M.
(Golden Empire Room, Mezzanine)

Thursday morning, May 3—9:30 A.M.–11:30 A.M.
(Golden Empire and Bonanza Rooms, Mezzanine)

Thursday afternoon, May 3—2:00 P.M.–4:00 P.M.
(Golden Empire and Bonanza Rooms, Mezzanine)

Industrial Electrolytic (Abstracts 107–121)

(All sessions in Peacock Court, Lobby)

Monday afternoon, April 30—2:15 P.M.–4:45 P.M.

Tuesday morning, May 1—9:30 A.M.–11:30 A.M.

Tuesday afternoon, May 1—2:00 P.M.–4:30 P.M.

Theoretical Electrochemistry (Abstracts 122–142)

(All sessions in the Room of the Dons, Lobby)

Wednesday morning, May 2—9:00 A.M.–12:00 M.

Wednesday afternoon, May 2—2:00 P.M.–5:00 P.M.

Thursday morning, May 3—9:30 A.M.–11:30 A.M.

Thursday afternoon, May 3—2:00 P.M.–4:30 P.M.

GENERAL INFORMATION

Convention Headquarters will be at the Hotel Mark Hopkins, California and Mason Streets, on Nob Hill, San Francisco, Calif.

Rates per day for rooms will be: single room: $10.00, 11.00, 12.00, 13.00, 14.00; double room: $14.00, 15.00, 16.00, 17.00, 18.00; suite: $25.00 to 40.00.

Requests for room reservations at the Headquarters Hotel should be made to the Reservation Department, Hotel Mark Hopkins, California and Mason Streets, San Francisco, Calif. Mention should be made of The Electrochemical Society.

Reservations for rooms have also been made at other hotels in San Francisco. Rates per day for rooms at these hotels will be:

Huntington, 1075 California St. (½ block from Mark Hopkins): single room $8.00–12.50; double room $8.00–15.00; twin-bed room $8.00–15.00; parlor suite $15.00–30.00.

Sir Francis Drake, 450 Powell St. (5 blocks from Mark Hopkins): single room $9.50–14.50; double room $11.50–16.50; twin-bed room $14.00–19.50; parlor suite $27.00–37.00.

Canterbury, 750 Sutter St. (5 blocks from Mark Hopkins): single room $6.00; double room $7.00; twin-bed room $10.00.

Chancellor, 433 Powell St. (5 blocks from Mark Hopkins): single room $5.75; double room $7.75; twin-bed room $8.75.

Requests for room reservations at these hotels should be made directly to the Reservation Department of the hotel concerned. Your name and address, a description of the accommodations desired, approximate arrival time, and date of departure should be given.

Mention should be made of The Electrochemical Society.

The office of the Secretary will be in the Phoenix Room on the Mezzanine Floor, Hotel Mark Hopkins.

Technical sessions will be held on the Lobby Floor and Mezzanine Floor of the Hotel, as designated in the program.

Ladies' Headquarters will be in the Conquistador Room on the Mezzanine Floor throughout the meeting. Most of the ladies' activities will originate here. For details see the program under Ladies' Program.

REGISTRATION

The registration desk will be located in the Lobby Writing Room in the Lobby of the Hotel. On Sunday, April 29, the registration desk will be open from 4:00 P.M. to 9:00 P.M. On Monday, Tuesday, and Wednesday, it will be open from 8:00 A.M. to 4:00 P.M.; on Thursday, from 8:00 A.M. to 12:00 M.

Registration fees are:

Members	$7.00
Ladies	$3.00
Students	$2.00
Nonmembers	$10.00

INFORMATION ABOUT SAN FRANCISCO

Since this is the first convention of The Electrochemical Society to be held in the West for many years, there will undoubtedly be a great interest in San Francisco, the San Francisco Bay Area, and the entire West Coast. The Society Convention Committee and the San Francisco Convention and Visitors Bureau are very anxious to assist, in any way they can, members and guests attending the convention to do any sightseeing, visiting, or vacationing they may desire. Booklets, pamphlets, and similar informative material will be available near the registration desk in the Lobby of the Hotel. However, it would be wise to make any arrangements requiring reservations as much ahead of time as possible. Accommodations at the many national parks and resort areas near San Francisco are in great demand. For prior assistance in these matters, consult your local travel agent or write direct to the San Francisco Convention and Visitors Bureau, Civic Auditorium, San Francisco 2, Calif.

ROUND-TABLE DISCUSSION AND SPECIAL SYMPOSIA

The Electric Insulation Division has scheduled a round table on "High Temperature Electrical Insulation, a New Frontier and a Challenge" at 3:00 P.M. on Tuesday, May 1, in the Golden Empire and Bonanza Rooms (Mezzanine).

The Corrosion and Theoretical Electrochemistry Divisions are sponsoring a symposium on "Adsorption Phenomena at Electrode Surfaces" all day Monday, April 30, and Tuesday morning, May 1, in the Bonanza Room (Mezzanine).

The Electronics Division, Semiconductor Group, has scheduled four symposia in the Peacock Court (Lobby): (*a*) Elemental Semiconductors, on Wednesday, May 2, at 9:00 A.M.; (*b*) Semiconducting Alloys and Compounds, on Wednesday, May 2, at 2:00 P.M.; (*c*) Process Technology, on Thursday, May 3, at 9:00 A.M.; (*d*) Surface Controlled Phenomena, on Thursday, May 3, at 2:00 P.M.

The Electrothermics and Metallurgy Division has scheduled five symposia: (*a*) Arcs in Inert Atmospheres and Vacuums, all day Monday and Tuesday, April 30 and May 1, in the Room of the Dons (Lobby); (*b*) Marginal Ores and Their Relationship to the National Economy, all day Monday, April 30, in the Golden Empire Room (Mezzanine); (*c*) Pyrometallurgical Refining of Reactor Fuels, on Wednesday morning, May 2, in the Golden Empire and Bonanza Rooms (Mezzanine); (*d*) Rare Earths, on Wednesday afternoon, May 2, in the Bonanza Room (Mezzanine); (*e*) Recent Developments in Super-refractories, on Wednesday afternoon, May 2, in the Golden Empire Room (Mezzanine) and all day Thursday, May 3, in the Golden Empire and Bonanza Rooms (Mezzanine).

The Industrial Electrolytic Division has scheduled two symposia in the Peacock Court (Lobby): (*a*) Electrowinning and General, on Monday afternoon, April 30; (*b*) Fused Salt Electrolysis, all day Tuesday, May 1.

BREAKFASTS, LUNCHEONS, AND DINNERS

Symposia Chairmen Breakfasts

On Monday, Tuesday, Wednesday, and Thursday, April 30, May 1, 2, and 3, at 7:45 A.M., special breakfasts for all symposia chairmen are being arranged in the Phoenix Room, Mezzanine ($2.00).

Monday, symposia chairmen for Corrosion—Theoretical Electrochemistry, Electric Insulation, Industrial Electrolytics, and Electrothermics and Metallurgy are requested to attend; **Tuesday,** Corrosion—Theoretical Electrochemistry, Electric Insulation, Industrial Electrolytics, and Electrothermics and Metallurgy; **Wednesday,** Theoretical Electrochemistry, Electronics, and Electrothermics and Metallurgy; **Thursday,** Theoretical Electrochemistry, Electronics, and Electrothermics and Metallurgy.

Monday Luncheon and Annual Business Meeting

The Electrochemical Society Luncheon and Annual Business Meeting will be held at 12:30 P.M. on April 30, in the Peacock Court (Lobby). An interesting speaker will be provided.

Monday Evening Buffet Supper and Entertainment

Monday evening, April 30, has been reserved for an informal get-acquainted gathering. Cocktails, at 6:30 P.M., followed by a buffet supper with floor show and entertainment will be in the Room of the Dons (Lobby).

Tuesday Evening Reception and Banquet

A reception for President and Mrs. H. H. Uhlig will be held at 6:30 P.M. in the Room of the Dons. Cocktails will be served followed by dinner in Peacock Court. President Uhlig will then deliver the Presidential Address. Dancing will follow.

PLANT TRIPS

Two plant trips have been scheduled for this meeting. Participation in these trips must be arranged for at the time of registration for the convention. Transportation tickets can be obtained at the same time.

Tuesday, May 1, 10:00 A.M.—An inspection of Stanford Research Institute in Menlo Park has been arranged. SRI is the second largest organization of its kind in the U. S. Several of the divisions and research groups will be visited. Two types of groups will be organized: one spending the majority of its time in electronic engineering and one spending the majority of its time in the chemistry and physics laboratories. Transportation will be by chartered bus from the Hotel Mark Hopkins.

Wednesday, May 2, 5:30 P.M.—An inspection of the Radiation Laboratory, University of California, in Berkeley, has been arranged. The tour will begin with a short orientation lecture. Five of the most interesting projects in the laboratory will then be visited. It will be possible to adapt the tours of the various groups to the particular interests represented in the group. Transportation will be by chartered bus from the Hotel Mark Hopkins ($1.25). Dinner will be served at the Faculty Club, University of California, at 6:30 P.M., at visitors' expense.

LADIES' PROGRAM

Ladies' Headquarters will be in the Conquistador Room on the Mezzanine Floor of the Hotel Mark Hopkins throughout the meeting. All ladies are requested to visit this headquarters and register for the program which has been arranged. The various features of the program have been designed to allow sufficient time for shopping and other individual activities, attendance at the

social functions of the general convention, and yet highlight some of the almost innumerable points of interest of San Francisco and the Bay Area.

Monday, April 30—After registration, coffee and doughnuts will be served in the Conquistador Room at 10:30 A.M. during a get-acquainted meeting and reviewing of the program. The Ladies' Committee will be present to answer any questions and help in any way. This will be followed by a Society Luncheon at 12:30, which the ladies are welcome to attend. At 2:00 P.M., a bus will leave from in front of the Mark to tour the city, returning around 5:00 P.M. A moderate charge of $3.35 per person will be made for this tour. In the evening, there will be the Buffet Supper and floor show, with cocktails at 6:30 P.M. and dinner at 7:30 P.M.

Tuesday, May 1—The ladies will have a Continental Breakfast at 9:15 A.M. in the Mural Room of the St. Francis Hotel. Virginia Worth's tour of the most unique and interesting shops of San Francisco will follow. The afternoon will be free. In the evening, the ladies should plan to attend the Reception and Banquet for President and Mrs. Uhlig with cocktails at 6:30 and dinner about 7:30.

Wednesday, May 2—A bus will leave from the Hotel Mark Hopkins sharply at 10:00 A.M. to visit the Rod McLellan Orchid Nursery, traveling along the most scenic route. Around 12:30 P.M., lunch will be served at the Alta Mira (or Valhalla Inn) in Sausalito; arrival back at the Mark about 3:00 P.M. Evening free.

Thursday, May 3—The ladies will have coffee and doughnuts or rolls in the Conquistador Room at 9:30 A.M. The entire day is left free for individual plans. Members of the Ladies' Committee will be available to assist in any way they can.

LUNCHEONS AND BUSINESS MEETINGS OF DIVISIONS

Industrial Electrolytic Division will hold a luncheon and business meeting on Tuesday, May 1, at 12:30 P.M. in the Peacock Court (Lobby). W. C. Gardiner will give the Chlor-Alkali Committee Report.

Electrothermics and Metallurgy Division will hold a luncheon and business meeting on Wednesday, May 2, at 12:30 P.M. in the Peacock Court (Lobby).

Electronics Division will hold a luncheon and business meeting on Thursday, May 3, at 12:30 P.M. in the Peacock Court (Lobby).

Theoretical Electrochemistry Division will hold a business meeting on Thursday, May 3, at 11:30 A.M. in the Room of the Dons (Lobby), following the last Technical Paper on Thursday morning.

BOARD AND COMMITTEE MEETINGS

Sunday, April 29, 10:00 A.M.—Meeting of the Ways and Means Committee in the Conquistador Room (Mezzanine).

Sunday, April 29, 2:00 P.M.—Meeting of the Board of Directors in the Conquistador Room (Mezzanine).

Monday, April 30, 5:00 P.M.—Meeting of the Council of Local Sections in the Conquistador Room (Mezzanine).

Monday, April 30, 5:00 P.M.—Meeting of the Editorial Staff in the Phoenix Room (Mezzanine).

Tuesday, May 1, 5:00 P.M.—Meeting of the Membership Committee in the Conquistador Room (Mezzanine).

Wednesday, May 2, 5:00 P.M.—Meeting of the Management and Editorial Committee of the Electronics Division in the Phoenix Room (Mezzanine).

Wednesday, May 2, 5:00 P.M.—Meeting of the Sustaining Membership Committee in the Conquistador Room (Mezzanine).

COST OF VARIOUS FUNCTIONS (other than registration)

Symposia Chairmen Breakfast	$2.00
Division Luncheons	$3.75
Monday Society Luncheon	$3.75
Monday Cocktails, Buffet, and Entertainment	
(single)	$7.00
(couple)	$11.00
Tuesday Reception, Cocktails, Banquet, and Dancing	
(single)	$7.00
(couple)	$11.00
Meal Package [includes one divisional luncheon (lady's ticket not included), Monday Society Luncheon, Monday Buffet, and Tuesday Reception and Banquet]	
(single)	$19.35
(couple)	$30.15
Plant Trip Transportation only (per person)	
Radiation Laboratory	$1.25
Stanford Research Institute	$1.25
Monday Ladies' Tour of San Francisco	$3.35

(Gratuities and taxes included in the above prices)

JOURNALS

Copies of the January, February, March, and April issues of the Journal of The Electrochemical Society will be available at the registration desk. The price of a single copy of the JOURNAL is $1.25 to members and $1.75 to nonmembers.

EXTENDED ABSTRACTS

The Electronics Division again is making available an extended abstract booklet containing 1000-word abstracts of most of the papers presented at the Division's San Francisco symposia. Copies of the booklet will be on sale at the registration desk for $2.00.

The Theoretical Electrochemistry Division is also making available an extended abstract booklet containing 1000-word abstracts of most of the papers to be given at the Corrosion—Theoretical Electrochemistry symposia and the Theoretical Electrochemistry symposia at the San Francisco Meeting. Copies of the booklet will be on sale at the registration desk for $2.00.

DISCUSSION

There will be no recordings made of oral discussions. Those contributing to the discussion of a paper and desiring their remarks published will be supplied by the symposium chairman with a printed form on which any discussion may be written. These forms should be given to the Secretary-Treasurer of the Division or to the Managing Editor of the JOURNAL after the session. The discussion will then be referred to the authors for reply. Written discussion should be submitted within two months following publication of any article in the JOURNAL.

A discussion section is published semiannually in the JOURNAL.

SLIDES AT TECHNICAL SESSIONS

The Board of Directors of the Society does not favor indiscriminate photographing of slides during technical sessions. It is requested that no such photographs be taken. Chairmen of technical sessions should administer this rule.

EMPLOYMENT POSTERS

Companies which desire to recruit employees at the San Francisco Meeting will have posters to this effect on a bulletin board near the registration desk.

Technical Program

Monday, April 30, 1956

9:00 A.M.—Formal Opening of the 109th Convention with Introduction by General Chairman R. F. Bechtold and Response by President H. H. Uhlig (Room of the Dons, Lobby).

CORROSION — THEORETICAL ELECTROCHEMISTRY

Joint Symposium

Monday, April 30, 1956

Adsorption Phenomena at Electrode Surfaces

with Ernest Yeager presiding

(BONANZA ROOM, Mezzanine)

10:00 A.M.—**"Survey of the Work on Polarization of Iron Electrodes in**

MEETING ROOM SCHEDULES

Meeting	Monday		Tuesday		Wednesday		Thursday	
	A.M.	P.M.	A.M.	P.M.	A.M.	P.M.	A.M.	P.M.
Corrosion—Theoretical Electrochemistry	D_2	D_2	D_2					
Electric Insulation	C	C	C	D				
Electronics—								
Luminescence					C	C	C	C
Semiconductors					A	A	A	A
Electrothermics and Metallurgy								
Ares in Inert Atmospheres	B	B	B	B				
Marginal Ores	D_1	D_1						
Pyrometallurgical Refining					D			
Rare Earths						D_2		
Superrefractories						D_1	D	D
Industrial Electrolytic		A	A	A				
Theoretical Electrochemistry					B	B	B	B

A = Peacock Court (Lobby).
B = Room of the Dons (Lobby).
C = Argonaut Room (Mezzanine).
D = Golden Empire and Bonanza Rooms (Mezzanine).
D_1 = Golden Empire Room (Mezzanine).
D_2 = Bonanza Room (Mezzanine).

Acid Solutions" (Invited paper) by K. F. Bonhoeffer, Max-Planck Institute for Physical Chemistry, Göttingen, Germany. (Abstract No. 1)

10:45 A.M.—"Adsorption of Polyelectrolytes on a Mercury Surface" (Invited paper) by D. C. Grahame and I. R. Miller, Dept. of Chemistry, Amherst College, Amherst, Mass. (Abstract No. 2)

11:30 A.M.—"Adsorption and Corrosion" (Invited paper) by Norman Hackerman, Dept. of Chemistry, University of Texas, Austin, Texas. (Abstract No. 3)

12:30 P.M.—Society Luncheon and Business Meeting in the Peacock Court (Lobby).

Corrosion—Theoretical Electrochemistry Joint Symposium

Monday, April 30, 1956

Adsorption Phenomena at Electrode Surfaces (cont'd)

with Norman Hackerman presiding

(BONANZA ROOM, Mezzanine)

2:00 P.M.—"The Heat and Surface Potential of Adsorption of Hydrogen on Mercury" (Invited paper) by J. O'M. Bockris and J. T. Law, John Harrison Lab. of Chemistry, University of Pennsylvania, Philadelphia, Pa. (Abstract No. 4)

2:45 P.M.—"Hydrogen Evolution Kinetics and the Thermionic Work Function" (Invited paper) by B. E. Conway and J. O'M. Bockris, John Harrison Lab. of Chemistry, University of Pennsylvania, Philadelphia, Pa. (Abstract No. 5)

3:30 P.M.—"Adsorption and Polarography" (Invited paper) by Paul Delahay, Dept. of Chemistry, Louisiana State University, Baton Rouge, La. (Abstract No. 6)

4:00 P.M.—"Anodic Oxidation of Various Metals at Very Low Current Densities" by H. Johansen, G. B. Adams, Jr., and Pierre Van Rysselberghe, Dept. of Chemistry, University of Oregon, Eugene, Oreg. (Abstract No. 7)

4:30 P.M.—"Inhibition of Iron Corrosion in Acid Solutions" by C. V. King and Eric Rau, Dept. of Chemistry, New York University, New York, N. Y. (Abstract No. 8)

Corrosion—Theoretical Electrochemistry Joint Symposium

Tuesday, May 1, 1956

Adsorption Phenomena at Electrode Surfaces (cont'd)

with J. T. Waber presiding

(BONANZA ROOM, Mezzanine)

9:00 A.M.—"Electrical Double Layer Capacity and Surface Areas of Metals" by Norman Hackerman and R. J. Brodd, Dept. of Chemistry, University of Texas, Austin, Texas. (Abstract No. 9)

9:30 A.M.—"Oxygen Overvoltage in Concentrated Acid Solutions, I. Perchloric Acid" by T. R. Beck and R. W. Moulton, University of Washington, Seattle, Wash. (Abstract No. 10)

10:00 A.M.—"Inhibitory Processes at the Dropping Mercury Electrode, I. Structure of the Adsorbed Layer of Pyridine" by L. Gierst and D. Bermane, Corrosion Lab., Massachusetts Institute of Technology, Cambridge, Mass. (Abstract No. 11)

10:30 A.M.—"Inhibitory Processes at the Dropping Mercury Electrode, II. Inhibition of the Discharge of PbO_2H^- by Pyridine" by L. Gierst and D. Bermane, Corrosion Lab., Massachusetts Institute of Technology, Cambridge, Mass. (Abstract No. 12)

11:00 A.M.—"Radio-Tracer Technique for Continuous Measurements, in Situ, of Adsorption from Solutions" by M. T. Simnad, Carnegie Institute of Technology, Schenley Park, Pittsburgh, Pa. (Abstract No. 13)

11:30 A.M.—"Kinetics of Silver-Silver Ion Exchange" by C. V. King and Ann-Mari Simonsen, Dept. of Chemistry, New York University, New York, N. Y. (Abstract No. 14)

ELECTRIC INSULATION

Monday, April 30, 1956

with D. A. Lupfer presiding

(ARGONAUT ROOM, Mezzanine)

10:00 A.M.—"Biological Insulating Materials" by R. N. Hazelwood, Donner Lab. of Biophysics and Medical Physics, University of California, Berkeley, Calif. (Abstract No. 15)

10:45 A.M.—"Dielectric Strength of Insulation Systems" by D. A. Lupfer, Dielectric Materials, Electronics Div., General Electric Co., Syracuse, N. Y. (Abstract No. 16)

11:20 A.M.—"Thermal Evaluation of Insulation" by E. L. Brancato, U. S. Naval Research Lab., Washington, D. C. (Abstract No. 17)

12:30 P.M.—Society Luncheon and Business Meeting in Peacock Court (Lobby).

Electric Insulation (cont'd)

Monday, April 30, 1956

with R. N. Hazelwood presiding

(ARGONAUT ROOM, Mezzanine)

2:00 P.M.—"Thermal Expansion of Filled Epoxy Resins" by J. E. Carey, Rigid Plastics Technical Service, Shell Chemical Corp, Union, N. J. (Abstract No. 18)

2:45 P.M.—"Electrical Properties of Epoxy Resins" by C. H. Klute, Shell Development Co., Emeryville, Calif. (Abstract No. 19)

3:30 P.M.—"Characteristics of Multilayer Dielectrics" by D. A. Lupfer, Dielectric Materials, Electronics Div., General Electric Co., Syracuse, N. Y. (Abstract No. 20)

4:15 P.M.—"Application of Insulators

and Window Problems in Vacuum Tubes at Microwave Frequencies" by E. T. Jaynes, W. W. Hansen Labs. of Physics, Stanford University, Stanford, Calif. (Abstract No. 21)

Electric Insulation (cont'd)

Tuesday, May 1, 1956

with E. L. Brancato presiding

(ARGONAUT ROOM, Mezzanine)

9:30 A.M.—"Effect of Voltage at Elevated Temperatures on Insulation Resistance of Ceramic Capacitors" by K. H. Brandt, Convair Div., General Dynamics Corp., San Diego, Calif. (Abstract No. 22)

10:15 A.M.—"Microstructure of Barium Titanates Ceramics" by I. E. Burkes and R. C. de Vries, Research Lab., General Electric Co., Schenectady, N. Y. (Abstract No. 23)

11:00 A.M.—"Phase Equilibria and Solid-State Reactions in the System of Talc-Clay" by J. A. Pask, Div. of Mineral Technology, University of California, Berkeley, Calif. (Abstract No. 24)

(Late papers to be announced at meeting.)

Electric Insulation (cont'd)

Tuesday, May 1, 1956

with Hans Thurnauer presiding

(GOLDEN EMPIRE AND BONANZA ROOMS Mezzanine)

2:00 P.M.—"Electrochemical Etching of High Purity Aluminum Capacitor Foil in Sodium Chloride Solutions" by G. H. Kissin and Gloria S. Murphy, Dept. of Metallurgical Research, Kaiser Aluminum & Chemical Corp., Spokane, Wash. (Abstract No. 25)

Round-Table Discussion

3:00 P.M.—Round-table discussion on **High Temperature Electrical Insulation, A New Frontier and a Challenge,** with Hans Thurnauer leading the discussion.

ELECTRONICS—LUMINESCENCE

Wednesday, May 2, 1956

with J. H. Schulman presiding

(ARGONAUT ROOM, Mezzanine)

9:10 A.M.—Keynote Address—"Potentialities and Difficulties in the Interpretation of the Kinetics of Luminescence" by M. Schön, Munich, Germany. (Abstract No. 26)

10:00 A.M.—"Radiation Resulting from the Recombination of Holes and Electrons in Silicon" by J. R. Haynes, Bell Telephone Labs., Inc., Murray Hill, N. J. (Abstract No. 27)

10:30 A.M.—"Physical Basis of a Multiphonon Process" by J. J. Markham, Zenith Radio Corp., Chicago, Ill. (Abstract No. 28)

11:00 A.M.—"Thermoluminescence of Manganese-Activated Calcium Fluoride" by R. J. Ginther and R. D. Kirk, U. S. Naval Research Lab., Washington, D. C. (Abstract No. 29)

11:20 A.M.—"Thermoluminescence of Titanium-Activated Lithium Silicates" by P. J. Pizzolato, U. S. Naval Research Lab., Washington, D. C. (Abstract No. 30)

Electronics—Luminescence (cont'd)

Wednesday, May 2, 1956

with J. H. Schulman presiding

(ARGONAUT ROOM, Mezzanine)

2:00 P.M.—"Preparation of the Selenides of Hydrogen and Zinc" by G. E. Crosby, Radio Corp. of America, Lancaster, Pa. (Abstract No. 31)

2:20 P.M.—"Preparation of the Copper-Activated Zinc Selenide Phosphor by the Dry Process" by G. E. Crosby, Radio Corp. of America, Lancaster, Pa. (Abstract No. 32)

2:40 P.M.—"Ultraviolet Fluorescence of Some Ternary Silicates Activated with Lead" by H. A. Klasens, A. H. Hoekstra, and A. P. M. Cox, Philips Research Lab., Eindhoven, Netherlands. (Abstract No. 33)

3:10 P.M.—"Alkali Compensated Silicate Phosphor" by G. E. Crosby, Radio Corp. of America, Lancaster, Pa. (Abstract No. 34)

3:30 P.M.—"An Automatic Recording Radiometer" by A. E. Martin, C. E. Meinheit, and F. W. Harjes, Sylvania Electric Products Inc., Bayside, N. Y. (Abstract No. 35)

3:45 P.M.—"Some Practical Aspects of Electrophoretic Deposition" by G. F. Kinney, Dept. of Chemical Engineering, U. S. Naval Postgraduate School, Monterey, Calif., and J. V. Festa, Microwave Tube Lab., Sylvania Electric Products Inc., Mountain View, Calif. (Abstract No. 36)

4:00 P.M.—"Influence of Convection and Other Factors in Fluorescent Screen Uniformity" by P. R. Myers, Lehigh University, Bethlehem, Pa., and C. T. Lattimer, RCA Victor Div., Radio Corp. of America, Marion, Ind. (Abstract No. 37)

Electronics—Luminescence (cont'd)

Thursday, May 3, 1956

with J. H. Schulman presiding

(ARGONAUT ROOM, Mezzanine)

9:00 A.M.—"Time Average Electroluminescence Output of Some Zinc Sulfide Phosphors" by Sol Nudelman, U. S. Naval Ordnance Lab., White Oak, Md., and University of Maryland, College Park, Md., and Frank Matossi, U. S. Naval Ordnance Lab., White Oak, Md. (Abstract No. 38)

9:20 A.M.—"Electroluminescence of Zinc Sulfo-Selenide Phosphors with Copper Activators and Halide Coactivators" by I. J. Hegyi, S. Larach, and R. E. Shrader, RCA Labs., Radio Corp. of America, Princeton, N. J. (Abstract No. 39)

9:45 A.M.—"Physicochemical Aspects of Electroluminescence of Zinc Sulfide Phosphors with Copper Activator" by S. Larach, R. E. Shrader, and I. J. Hegyi, RCA Labs., Radio Corp. of America, Princeton, N. J. (Abstract No. 40)

10:00 A.M.—"Further Experiments on Electroluminescence of ZnS Single Crystals" by D. R. Frankl, Physics Lab., Sylvania Electric Products Inc., Bayside, N. Y. (Abstract No. 41)

10:40 A.M.—"A Theory of the Electroluminescence of ZnS Single Crystals" by J. L. Birman, Physics Lab., Sylvania Electric Products Inc., Bayside, N. Y. (Abstract No. 42)

11:10 A.M.—"Some Experiments on Persistent Polarization and Photoconductivity in ZnS Crystals" by A. Lempicki, Physics Lab., Sylvania Electric Products Inc., Bayside, N. Y. (Abstract No. 43)

12:30 P.M.—Electronics Division Luncheon and Business Meeting in the Peacock Court (Lobby).

Electronics—Luminescence (cont'd)

Thursday, May 3, 1956

with J. H. Schulman presiding

(ARGONAUT ROOM, Mezzanine)

2:00 P.M.—"Incorporation of Chloride in ZnS Phosphor Preparation" by A. Kremheller, A. K. Levine, and D. J. Bracco, Sylvania Electric Products Inc., Flushing, N. Y. (Abstract No. 44)

2:30 P.M.—"The Release of Chloride from Zinc Sulfide by Grinding" by A. Kremheller and A. K. Levine, Sylvania Electric Products Inc., Flushing, N. Y. (Abstract No. 45)

ELECTRONICS—SEMICONDUCTORS

Wednesday, May 2, 1956

Elemental Semiconductors

with G. K. Teal presiding

(PEACOCK COURT, Lobby)

9:00 A.M.—Introductory Remarks by J. W. Faust, Jr.

9:10 A.M.—Keynote Address—"Surface States on Semiconductors" by J. Bardeen, University of Illinois, Urbana, Ill. (Abstract No. 46)

9:40 A.M.—"Elemental Semicon-

ductors" by H. Y. Fan, Purdue University, Lafayette, Ind. (Abstract No. 47)

10:10 A.M.—"Defects in Crystals of Silicon and Germanium Grown from the Melt" by E. Billig, Associated Electrical Industries, Aldermaston, England. (Abstract No. 48)

10:40 A.M.—"Rectifying Semiconductor Contacts—A Review of Theoretical Progress" by H. K. Henisch, Sylvania Electric Products Inc., Bayside, N. Y., and Reading University, England. (Abstract No. 49)

11:20 A.M.—"Distribution of Copper between Germanium and Ternary Melts Saturated with Germanium" by C. D. Thurmond and R. A. Logan, Bell Telephone Labs., Inc., Murray Hill, N. J. (Abstract No. 50)

Electronics—Semiconductors (cont'd)

Wednesday, May 2, 1956

Semiconducting Alloys and Compounds

with A. Beer presiding

(PEACOCK COURT, Lobby)

2:00 P.M.—"Conductivity and Band Gap Measurements of Some Relatives of Phthalocyanine" by Wolfgang Felmayer and Irving Wolf, General Electric Co., Syracuse, N. Y. (Abstract No. 51)

2:30 P.M.—"Ternary Compound Semiconductors with the Chalcopyrite Structure" by I. G. Austin, C. H. L. Goodman, and A. E. S. Pengelly, The General Electric Co., Ltd., Wembley, England. (Abstract No. 52)

2:45 P.M.—"Electronic and Ionic Fluctuation Processes in Semiconductors" by R. E. Burgess, Dept. of Physics, University of British Columbia, Vancouver, B.C., Canada. (Abstract No. 53)

3:15 P.M.—"Influence of the Absorption Edges of Cadmium and Silver on the X-Ray Diffraction Pattern of Cadmium Compounds" by R. J. Robinson and F. Schossberger, Armour Research Foundation of Illinois Institute of Technology, Chicago, Ill. (Abstract No. 54)

3:45 P.M.—"Recent News" Papers. Titles and short abstracts will be available at the registration desk.

Electronics—Semiconductors (cont'd)

Thursday, May 3, 1956

Process Technology

with H. Q. North presiding

(PEACOCK COURT, Lobby)

9:00 A.M.—"The Status of Semiconductor Technology" by F. J. Biondi, Bell Telephone Labs., Inc., Murray Hill, N. J. (Abstract No. 55)

9:30 A.M.—"A Metal-Semiconductor Capacitor" by R. L. Taylor and H. E. Haring, Bell Telephone Laboratories, Inc., Murray Hill, N. J. (Abstract No. 56)

10:00 A.M.—"Design of Diffused Junction Silicon Diodes" by H. S. Veloric and K. D. Smith, Bell Telephone Labs., Inc., Murray Hill, N. J. (Abstract No. 57)

10:30 A.M.—"Recent News" Papers. Titles and short abstracts will be available at the registration desk.

12:30 P.M.—Electronics Division Luncheon and Business Meeting in the Peacock Court (Lobby).

Electronics—Semiconductors (cont'd)

Thursday, May 3, 1956

Surface Controlled Phenomena

with A. E. Middleton presiding

(PEACOCK COURT, Lobby)

2:00 P.M.—"Some Applications of Field Effect Studies on Germanium Surfaces" by E. N. Clarke, Physics Lab., Sylvania Electric Products Inc., Bayside, N. Y. (Abstract No. 58)

2:30 P.M.—"Anodic Oxidation of Silicon" by P. F. Schmidt, Philco Corp., Philadelphia, Pa. (Abstract No. 59)

3:00 P.M.—"Anodic Oxide Films on Germanium" by Solomon Zwerdling and Sumner Sheff, Lincoln Lab., Massachusetts Institute of Technology, Lexington, Mass. (Abstract No. 60)

3:30 P.M.—"Recent News" Papers. Titles and short abstracts will be available at the registration desk.

ELECTROTHERMICS AND METALLURGY

Monday, April 30, 1956

Arcs in Inert Atmospheres and Vacuum—Arc Characteristics and Theory

with W. E. Kuhn presiding

(ROOM OF THE DONS, Lobby)

10:00 A.M.—Introductory Remarks by W. E. Kuhn, Research and Development Div., Carborundum Co. Inc., Niagara Falls, N. Y.

10:20 A.M.—"Characteristics of High Current Arcs for Consumable Electrode Arc Melting" by F. W. Wood and R. A. Beall, U. S. Bureau of Mines, Albany, Oreg. (Abstract No. 61)

10:50 A.M.—"Energy Transfer in the High Intensity Arc" by Lawrence Mead, Marilyn A. Marquis, Charles Sheer, and Samuel Korman, Arc Research Dept., Vitro Labs., Vitro Corp. of America, West Orange Lab., West Orange, N. J. (Abstract No. 62)

11:20 A.M.—"A Descriptive Study of Consumable Electrode Arcs; the Pressure Dependence of Their Mode of Burn-Off—A Film" by F. W. Wood and R. A. Beall, U. S. Bureau of Mines, Albany, Oreg. (Abstract No. 63)

12:30 P.M.—Society Luncheon and Business Meeting in Peacock Court (Lobby Floor).

Electrothermics and Metallurgy

Monday, April 30, 1956

Arcs in Inert Atmospheres and Vacuum—Arc Characteristics and Theory (cont'd)

with P. C. Rossin presiding

(ROOM OF THE DONS, Lobby)

2:15 P.M.—"Effects of Magnetic Stirring on Titanium Ingot Quality" by D. E. Cooper and R. J. Krieger, Titanium Metals Corp. of America, Henderson, Nev. (Abstract No. 64)

2:45 P.M.—"Properties of the Anode Flame of the High Intensity Arc" by Marilyn A. Marquis, Lawrence Mead, Samuel Korman, and Charles Sheer, Arc Research Dept., Vitro Labs., Vitro Corp. of America, West Orange Lab., West Orange, N. J. (Abstract No. 65)

3:15 P.M.—"Characteristics of Consumable Electrode D-C Arcs in Argon" by E. W. Johnson and G. T. Hahn, Research Labs., Westinghouse Electric Corp., Pittsburgh, Pa. (Abstract No. 66)

3:45 P.M.—"The Effect of Variables on the Melting Rate of Metals in the Consumable Electrode Arc Furnace" by W. H. Smith and R. M. Parke, Research Lab., General Electric Co., Schenectady, N. Y. (Abstract No. 67)

Electrothermics and Metallurgy

Tuesday, May 1, 1956

Arcs in Inert Atmospheres and Vacuum—Arc Characteristics and Theory (cont'd)

with A. U. Seybolt presiding

(ROOM OF THE DONS, Lobby)

9:00 A.M.—"The High Intensity Arc in Process Chemistry" by Charles Sheer and Samuel Korman, Arc Research Dept., Vitro Labs., Vitro Corp. of America, West Orange Lab., West Orange, N. J. (Abstract No. 68)

9:30 A.M.—"Arc Melting in a Vacuum" by G. W. P. Rengstorff, Battelle Memorial Institute, Columbus, Ohio. (Abstract No. 69)

10:00 A.M.—"Vacuum Remelting of Superalloys and Steels by the Consumable Electrode Process" by

W. W. Dyrkacz, Allegheny Ludlum Steel Corp., Watervliet, N. Y. (Abstract No. 70)

10:30 A.M.—"Arc Properties in the Five Rare Gases" by H. S. Morton and R. M. Gage, Linde Air Products Co., A Division of Union Carbide and Carbon Corp., Tonawanda, N. Y. (Abstract No. 71)

Electrothermics and Metallurgy (cont'd)

Tuesday, May 1, 1956

Arcs in Inert Atmospheres and Vacuum—Furnace Design, Operation, and Applications

with E. W. Johnson presiding

(ROOM OF THE DONS, Lobby)

2:00 P.M.—"A Pilot Model Three-Phase A-C Consumable-Electrode Arc Furnace" by P. C. Magnusson, G. L. Schmidt, F. Caputo, and R. A. Beall, U. S. Bureau of Mines, Albany, Oreg. (Abstract No. 72)

2:30 P.M.—"A Vacuum Arc Melting Furnace for Refractory Metals" by O. Z. Rylski and H. V. Kinsey, Physical Metallurgy Div., Dept. of Mines and Technical Surveys, Ottawa, Ont., Canada. (Abstract No. 73)

3:00 P.M.—"Electrode Control Systems for Inert Atmosphere and Vacuum Furnaces" by E. J. Borreback, Industrial Engineering Dept., Westinghouse Electric Corp., East Pittsburgh, Pa. (Abstract No. 74)

3:30 P.M.—"The High Intensity Arc: Electrode Requirements for Metallurgical Applications" by Samuel Korman and Charles Sheer, Arc Research Dept., Vitro Labs., Vitro Corp. of America, West Orange, N. J. (Abstract No. 75)

Electrothermics and Metallurgy (cont'd)

Monday, April 30, 1956

Marginal Ores and Their Relationship to the National Economy

with A. H. Roberson presiding

(GOLDEN EMPIRE ROOM, Mezzanine)

10:00 A.M.—Introductory Remarks by S. M. Shelton.

10:10 A.M.—"A New Concept of Treating High Iron Bauxites in the Electric Furnace" by M. J. Udy, Strategic-Udy Metallurgical Processes Ltd., Niagara Falls, Ont., Canada. (Abstract No. 76)

10:35 A.M.—"Utilization of Siliceous Manganese Ores for Production of Silicomanganese" by W. E. Anable, U. S. Bureau of Mines, Albany, Oreg. (Abstract No. 77)

11:00 A.M.—"The Use of Waste Carbonaceous Materials in Electric Smelting" by R. R. Rogers and G. E. Viens, Dept. of Mines and Technical Surveys, Ottawa, Ont., Canada. (Abstract No. 78)

11:30 A.M.—"Alaska's Power Resources in Relation to Mineral Development" by Ivan Bloch, Ivan Bloch and Associates, 611 Park Bldg., Portland, Oreg. (Abstract No. 79)

12:30 P.M.—Society Luncheon and Business Meeting in Peacock Court (Lobby).

Electrothermics and Metallurgy

Monday, April 30, 1956

Marginal Ores and Their Relationship to the National Economy (cont'd)

with A. H. Roberson presiding

(GOLDEN EMPIRE ROOM, Mezzanine)

2:15 P.M.—"Production of Thorium" by T. C. Runion and F. L. Cuthbert, National Lead Co. of Ohio, Cincinnati, Ohio. (Abstract No. 80)

2:45 P.M.—"Problems in the Extraction of Thorium and Rare Earth from Ores" by H. E. Kremers, Lindsay Chemical Co., West Chicago, Ill. (Abstract No. 81)

3:15 P.M.—"Processing of Alluvial Sands for the Recovery of Tantalum-Columbium Bearing Minerals" by J. E. Shelton, U. S. Dept. of the Interior, Bureau of Mines, Albany, Oreg. (Abstract No. 82)

3:45 P.M.—"Electrodeposition of Molybdenum" by T. T. Campbell, U. S. Dept. of the Interior, Bureau of Mines, Albany, Oreg. (Abstract No. 83)

Electrothermics and Metallurgy (cont'd)

Wednesday, May 2, 1956

Pyrometallurgical Refining of Reactor Fuels

with Daniel Cubicciotti presiding

(GOLDEN EMPIRE AND BONANZA ROOMS, Mezzanine)

9:00 A.M.—"Separation of Plutonium from Uranium by Distillation, Magnesium Extraction, and Salt Extraction" by R. A. Barney, A. G. Buyers, D. Cubicciotti, F. J. Keneshea, A. Saul, and S. J. Yosim, Atomics International, Canoga Park, Calif. (Abstract No. 84)

9:30 A.M.—"Precipitation Processes for Liquid Metal Fuels and Breeders" by R. J. Teitel, Metallurgy Dept., Brookhaven National Lab., Upton, N. Y. (Abstract No. 85)

10:00 A.M.—"Melt Refining of Uranium Metal" by H. M. Feder, L. Burris, and N. Chellew, Argonne National Lab., Lemont, Ill. (Abstract No. 86)

10:30 A.M.—"Uranium Hexafluoride Distillation" by R. K. Steunenberg, Argonne National Lab., Lemont, Ill. (Abstract No. 87)

11:00 A.M.—"Uranium Purification by Electrorefining" by L. W. Niedrach and A. C. Glamm, Knolls Atomic Power Lab., Schenectady, N. Y. (Abstract No. 88)

11:30 A.M.—"Liquid Metal Extraction of Reactor Fuels" by A. F. Voigt, F. H. Spedding, A. H. Daane, and Others, Institute for Atomic Research, Iowa State College, Ames, Iowa. (Abstract No. 89)

12:30 P.M.—Electrothermics and Metallurgy Division Luncheon and Business Meeting in the Peacock Court (Lobby). Speaker to be announced.

Electrothermics and Metallurgy (cont'd)

Wednesday, May 2, 1956

Rare Earths

with W. H. Smith presiding

(BONANZA ROOM, Mezzanine)

2:00 P.M.—"Metallurgy and Physical Properties of Rare Earth Metals" by F. H. Spedding, Iowa State College, Ames, Iowa. (Abstract No. 90)

2:30 P.M.—"Flame Spectra of Some Rare Earths" by A. W. Berger and T. F. Powers, Heavy Minerals Co., Chicago, Ill. (Abstract No. 91)

3:00 P.M.—"A Caustic Process for the Treatment of Monazite and Xenotime" by Paul Kruesi, Heavy Minerals Co., Chicago, Ill. (Abstract No. 92)

3:30 P.M.—"Equilibrium and Kinetic Studies on the Praseodymium Oxide System" by C. L. Sieglaff and L. Eyring, State University of Iowa, Iowa City, Iowa. (Abstract No. 93)

4:00 P.M.—"Studies on Complex Formation in Lanthanon Aliphatic Carboxylates" by R. C. Vickery, Horizons Inc., Cleveland, Ohio. (Abstract No. 94)

Electrothermics and Metallurgy (cont'd)

Wednesday, May 2, 1956

Recent Developments in Super-refractories

with Winston Duckworth presiding

(GOLDEN EMPIRE ROOM, Mezzanine)

2:00 P.M.—"High Temperature Material Requirements in the Air Force" by R. A. Jones, Materials Branch, Equipment Div., Air Research and Development Command, USAF, Baltimore, Md. (Abstract No. 95)

2:30 P.M.—"Recent Navy Evaluations of Ceramic and Cermet Materials" by H. Hessing, Bureau of Aeronautics, Navy Dept., Washington, D. C., J. J. Harwood, Metallurgy Branch, Office of Naval Research, Navy Dept., Washington, D. C., and J. F. Erthal, Mechanical Properties Branch, Aeronautical Materials Lab.,

Naval Air Material Center, Philadelphia, Pa. (Abstract No. 96)

3:00 P.M.—"Defect Structure and the Temperature Dependence of Strength of an Intermetallic Compound" by J. H. Westbrook, Research Lab., General Electric Co., Schenectady, N. Y. (Abstract No. 97)

3:30 P.M.—"The Elastic Properties of Super-refractory Materials by a Sonic Method" by S. M. Lang, Porcelain and Pottery Section, National Bureau of Standards, Washington, D. C. (Abstract No. 98)

Electrothermics and Metallurgy

Thursday, May 3, 1956

Recent Developments in Super-refractories (cont'd)

with Winston Duckworth presiding

(GOLDEN EMPIRE AND BONANZA ROOMS, Mezzanine)

9:30 A.M.—"KT Silicon Carbide; A New High-Density Silicon Carbide Body" by K. M. Taylor, The Carborundum Co., Niagara Falls, N. Y. (Abstract No. 99)

10:00 A.M.—"Infiltrated Titanium Carbide—An Improved Cermet for Turbine Bladings" by C. G. Goetzel, Sintercast Corp. of America, Yonkers, N. Y. (Abstract No. 100)

10:30 A.M.—"The Effect of Particle Size on the Bulk Density and Strength Properties of Uranium Dioxide Specimens" by M. D. Burdick and H. S. Parker, Porcelain and Pottery Section, National Bureau of Standards, Washington, D. C. (Abstract No. 101)

11:00 A.M.—"Some Physical Properties of High-Density Thorium Dioxide" by S. M. Lang and F. P. Knudsen, Porcelain and Pottery Section, National Bureau of Standards, Washington, D. C. (Abstract No. 102)

Electrothermics and Metallurgy

Thursday, May 3, 1956

Recent Developments in Super-refractories (cont'd)

with Winston Duckworth presiding

(GOLDEN EMPIRE AND BONANZA ROOMS, Mezzanine)

2:00 P.M.—" 'Rockide' Coatings for Jet Nozzles" by W. L. Howe, Norton Co., Worcester, Mass. (Abstract No. 103)

2:30 P.M.—"The Status of Carbides, Borides, Cermets, and Intermetallics for High Temperature Service" by M. F. Judkins, New Products Div., Firth Sterling, Inc., Pittsburgh, Pa. (Abstract No. 104)

3:00 P.M.—"Use of Cermets as Turbine Blades" by G. C. Deutsch, Lewis Flight Propulsion Lab., Cleveland, Ohio (Abstract No. 105)

3:30 P.M.—"Use of Super-refractories in Rocket Thrust Chambers" by W. R. Sheridan, Rocket Materials and Propellants, Bell Aircraft Corp., Buffalo, N. Y. (Abstract No. 106)

INDUSTRIAL ELECTROLYTIC

Monday, April 30, 1956

Electrowinning and General

with W. D. Sherrow presiding

(PEACOCK COURT, Lobby)

2:15 P.M.—"A Commercial Process for Electrowinning Manganese" by M. C. Carosella and R. M. Fowler, Electro Metallurgical Co., A Division of Union Carbide and Carbon Corp., Niagara Falls, N. Y. (Abstract No. 107)

2:45 P.M.—"Current Efficiency of Anodic Oxide Coating Formation on Commercial Aluminum Alloys" by G. H. Kissin and R. V. Paulson, Dept. of Metallurgical Research, Kaiser Aluminum & Chemical Corp., Spokane, Wash. (Abstract No. 108)

3:15 P.M.—"The Structure of Kanigen" by A. W. Goldenstein, G. Gutzeit, W. Rostocker, and F. Schossberger, Armour Research Foundation of Illinois Institute of Technology, Chicago, Ill. (Abstract No. 109)

3:45 P.M.—"Studies of a Vertical Rotary Mercury Cathode Cell" by Shinzo Okada and Shiro Yoshizawa, Dept. of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yosida, Kyoto, Japan. (Abstract No. 110)

4:15 P.M.—"Electrolytic Production of Bromates" by Takashi Osuga and Kiichiro Sugino, Sanwa Pure Chemicals Co. and Tokyo Institute of Technology, Tokyo, Japan. (Abstract No. 111)

Industrial Electrolytic (cont'd)

Tuesday, May 1, 1956

Fused Salt Electrolysis

with Milton Janes presiding

(PEACOCK COURT, Lobby)

9:30 A.M.—"Polarization in an Aluminum Reduction Cell" by W. E. Haupin, Aluminum Research Labs., Aluminum Co. of America, New Kensington, Pa. (Abstract No. 113)

10:00 A.M.—"Relation of Current Efficiency to Gas Composition in Aluminum Reduction Cells" by T. R. Beck, Chemical Research Dept., Kaiser Aluminum & Chemical Corp., Permanente, Calif. (Abstract No. 114)

10:30 A.M.—"Electrolytic Preparation of Thorium-Bismuthide Dispersions in Bismuth for Blanket Preparation in the LMFR" by M. A. Steinberg and M. E. Sibert, Horizons Inc., Cleveland, Ohio, and R. J. Teitel, Brookhaven National Labs., Upton, N. Y. (Abstract No. 115)

11:00 A.M.—"Evaluation of Electrolytic Parameters in the Preparation of Thorium Metal by Fused Salt Electrolysis" by J. C. Bleiweiss, B. C. Raynes, and M. A. Steinberg, Horizons Inc., Cleveland, Ohio. (Abstract No. 116)

12:30 P.M.—Industrial Electrolytic Division Luncheon and Business Meeting, Peacock Court (Lobby). W. C. Gardiner will give the Chlor-Alkali Committee Report.

Industrial Electrolytic

Tuesday, May 1, 1956

Fused Salt Electrolysis (cont'd)

with J. C. Schumacher presiding

(PEACOCK COURT, Lobby)

2:00 P.M.—"The Mobility of the Ions in Silver Nitrate-Alkali Nitrate Mixtures" by F. R. Duke, Nobel Ida, and Boone Owens, Iowa State College of Agriculture and Mechanic Arts, Ames, Iowa. (Abstract No. 117)

2:30 P.M.—"The Mechanism of Titanium Production by Electrolysis of Fused Halide Baths Containing Titanium Salts" by J. G. Wurm, Lucien Gravel, and R. J. A. Potvin, Laval University, Quebec, Que., Canada. (Abstract No. 118)

3:00 P.M.—"The Electrorefining of Titanium in Fused Salt Media" by D. H. Baker, Jr., and J. R. Nettle, Electrometallurgical Experiment Station, Bureau of Mines, U. S. Dept. of the Interior, Boulder City, Nev. (Abstract No. 119)

3:30 P.M.—"The Mechanism of Deposition of Titanium Coatings from Fused Salt Baths" by M. E. Straumanis, S. T. Shih, and A. W. Schlechten, Dept. of Metallurgy, University of Missouri School of Mines and Metallurgy, Rolla, Mo. (Abstract No. 120)

4:00 P.M.—"Deposition of Titanium from Titanium-Oxygen Alloys on Copper, Iron, and Mild Steel" by S. T. Shih, M. E. Straumanis, and A. W. Schlechten, Dept. of Metallurgy, University of Missouri School of Mines and Metallurgy, Rolla, Mo. (Abstract No. 121)

Joint Symposium

THEORETICAL ELECTROCHEMISTRY AND CORROSION

Monday, April 30, Tuesday, May 1, 1956

Adsorption Phenomena at Electrode Surfaces

(BONANZA ROOM, Mezzanine)

See Corrosion-Theoretical Electrochemistry, Joint Symposium, page 49C.

THEORETICAL ELECTROCHEMISTRY

Wednesday, May 2, 1956

with Ernest Yeager presiding

(ROOM OF THE DONS, Lobby)

9:00 A.M.—"A Study of the Cathodic Reduction of Oxide Films on Iron, II. The Reduction of Magnetite" by H. G. Oswin, Dept. of Metallurgical Research, Kaiser Aluminum & Chemical Corp., Spokane, Wash. (Abstract No. 122)

9:30 A.M.—"Mechanisms of Hydrogen Producing Reactions on Palladium, II. Diffusion of Electrolytic Hydrogen through Palladium" by Sigmund Schuldiner and J. P. Hoare, Naval Research Lab., Washington, D. C. (Abstract No. 123)

10:00 A.M.—"Mechanisms of Hydrogen Producing Reactions on Palladium, III. Hydrogen Overvoltage on the Polarization and Diffusion Sides of a Cathode-Diaphragm" by J. P. Hoare and Sigmund Schuldiner, Naval Research Lab., Washington, D. C. (Abstract No. 124)

10:30 A.M.—"Mechanisms of Hydrogen Producing Reactions on Palladium, IV. Potential of the Alpha-Palladium/Hydrogen Electrode" by Sigmund Schuldiner and J. P. Hoare, Naval Research Lab., Washington, D. C. (Abstract No. 125)

11:00 A.M.—"Comparison of the Variations of the Direct Method of Measuring Polarization, I. Potentiometric Study with Copper Electrodes in Acid Copper Sulfate Solution" by A. L. Ferguson and L. O. Case, University of Michigan, Ann Arbor, Mich., and R. S. Karpiuk, Dow Chemical Co., Midland, Mich. (Abstract No. 126)

11:30 A.M.—"Comparison of the Variations of the Direct Method of Measuring Polarization, II. Oscillographic Study with Copper Electrodes in Acid Copper Sulfate Solution" by A. L. Ferguson and L. O. Case, University of Michigan, Ann Arbor, Mich., and R. S. Karpiuk, Dow Chemical Co., Midland, Mich. (Abstract No. 127)

Theoretical Electrochemistry (cont'd)

Wednesday, May 2, 1956

with Sigmund Schuldiner presiding

(ROOM OF THE DONS, Lobby)

2:00 P.M.—"Hydrogen Overvoltage on Lead" by Edward Kure, Ernest Yeager, and Frank Hovorka, Dept. of Chemistry, Western Reserve University, Cleveland, Ohio. (Abstract No. 128)

2:30 P.M.—"Hydrogen Overvoltage on Nickel" by Richard Jefferys, Ernest Yeager, and Frank Hovorka, Dept. of Chemistry, Western Reserve University, Cleveland, Ohio. (Abstract No. 129)

3:00 P.M.—"Molecular Desorption as a Rate-Determining Step for Hydrogen Overvoltage on Platinum" by Gerald Lozier, Ernest Yeager, and Frank Hovorka, Dept. of Chemistry, Western Reserve University, Cleveland, Ohio. (Abstract No. 130)

3:30 P.M.—"Nitrogen Overpotential on Bright Platinum in Liquid Ammonia Solutions" by Morris Eisenberg, Stanford Research Institute, Menlo Park, Calif. (Abstract No. 131)

4:00 P.M.—"High Current Electronic Interrupter for the Study of Electrode Processes" by W. E. Richeson and Morris Eisenberg, Stanford Research Institute, Menlo Park, Calif. (Abstract No. 132)

4:30 P.M.—"Diffusion-Controlled Metal Deposition on Stationary Microelectrodes" by T. Pavlopoulos and J. D. H. Strickland, British Columbia Research Council, University of British Columbia, Vancouver, B.C., Canada. (Abstract No. 133)

Theoretical Electrochemistry (cont'd)

Thursday, May 3, 1956

with C. V. King presiding

(ROOM OF THE DONS, Lobby)

9:30 A.M.—"Problems of Electrochemical Nomenclature and Definitions" by Pierre Van Rysselberghe, Dept. of Chemistry, University of Oregon, Eugene, Oreg. (Abstract No. 134)

10:00 A.M.—"Mathematical Studies on Galvanic Corrosion, V. Calculation of the Average Value of the Corrosion Current Parameter" by J. T. Waber, John Morrissey, and John Ruth, Los Alamos Scientific Lab., University of California, Los Alamos, N. Mex. (Abstract No. 135)

10:30 A.M.—"The Anode Behavior of Germanium in Aqueous Solutions" by D. R. Turner, Bell Telephone Labs., Inc., Murray Hill, N. J. (Abstract No. 136)

11:00 A.M.—"Electrokinetic Potentials on Bulk Metals by Streaming Current Measurements, II. Gold, Platinum, and Silver in Dilute Aqueous Electrolytes" by R. M. Hurd and Norman Hackerman, Defense Research Lab. and Dept. of Chemistry, University of Texas, Austin, Texas. (Abstract No. 137)

11:30 A.M.—Theoretical Electrochemistry Division Business Meeting.

Theoretical Electrochemistry (cont'd)

Thursday, May 3, 1956

with C. V. King presiding

(ROOM OF THE DONS, Lobby)

2:00 P.M.—"Electrolytes of Binary Solutes in Ketones" by J. E. Lilienfeld, Helen Y. Hsiao, and H. S. Myers, Power Condenser and Electronics Corp., Washington, D. C. (Abstract No. 138)

2:30 P.M.—"The Allotropic Modifications of Calcium" by J. F. Smith, O. N. Carlson, and R. W. Vest, Institute for Atomic Research and Dept. of Chemistry, Iowa State College, Ames, Iowa. (Abstract No. 139)

3:00 P.M.—"A Proposed Mechanism for the Electrolytic Conductance of Soda-Silica Glasses" by A. B. Rothman, Research Labs., Pittsburgh Plate Glass Co., Creighton, Pa. (Abstract No. 140)

3:30 P.M.—"Electrochemical Properties of a Cation-Transfer Membrane" by N. W. Rosenberg, J. H. B. George, and W. D. Potter, Ionics, Inc., Cambridge, Mass. (Abstract No. 141)

4:00 P.M.—"Electrochemistry Applied to Electrophysiology" by R. H. Beutner, Medical Research Lab., Des Moines Still College of Osteopathy and Surgery, Des Moines, Iowa. (Abstract No. 142)

ABSTRACTS

CORROSION — THEORETICAL ELECTROCHEMISTRY

Abstract No. 1

SURVEY OF THE WORK ON POLARIZATION OF IRON ELECTRODES IN ACID SOLUTIONS

K. F. Bonhoeffer

The report is restricted to polarization phenomena on pure iron in acid solutions of $pH < 4$ which contain neither oxygen nor other depolarizers. Higher anodic polarization currents leading to surface layers or passivity are excluded from consideration. Based on new experiments of Kaesche, anodic hysteresis phenomena are discussed in detail. It is suggested the adsorbed and dis-

solved hydrogen is responsible for these effects.

Abstract No. 2

ADSORPTION OF POLYELECTROLYTES ON A MERCURY SURFACE

D. C. Grahame and I. R. Miller

Differential capacities of the electrical double layer at the boundary between mercury and aqueous solutions of 0.09*N* $NaClO_4$ + 0.01*N* $HClO_4$ containing various concentrations of polymethacrylic acid have been measured. Results indicate the existence at the interface of a "surface phase" composed of molecules bound to the metal by a multiplicity of individually weak bonds. The act of forming and breaking these bonds involves an activation energy presumed to be related to the associated reorientation of the adsorbed molecules.

Abstract No. 3

ADSORPTION AND CORROSION

Norman Hackerman

In corrosion reactions of adsorption a foreign substance may interfere with material transport or alter the activity of the metal. In the first case, the effect on open-circuit potential should be small, although there might be a major influence on polarization of a gas-producing reaction. In the second case, the effect on open-circuit potential should be larger. "Surface complexes" are discussed in some detail in terms of the above effects.

Abstract No. 4

THE HEAT AND SURFACE POTENTIAL OF ADSORPTION OF HYDROGEN ON MERCURY

J. O'M. Bockris and J. T. Law

The heat of adsorption of hydrogen and the dipolar nature of the metal-hydrogen bond are of considerable importance in the evaluation of the heat of activation in the hydrogen evolution reaction. These quantities have been measured under conditions of high purity at an Hg surface, and the results applied to the elucidation of the mechanism of proton discharge.

Abstract No. 5

HYDROGEN EVOLUTION KINETICS AND THE THERMIONIC WORK FUNCTION

B. E. Conway and J. O'M. Bockris

The rate of hydrogen evolution at electrodes increases with the electronic work function. Desorption rates would, however, be expected to decrease with increasing hydrogen adsorption energy. The anomaly is explained by the dependence of hydrogen adsorption energy on coverage and by proton diffusion through the metal surface with metallic orbital formation by the hydrogen electron with the metal *d*-bands. The model indicates the distribution of mechanisms for the hydrogen evolution reaction as a function of the *d*-band character of the metal substrate.

Abstract No. 6

ADSORPTION AND POLAROGRAPHY

Paul Delahay

Some characteristics of electrode processes with partial or total diffusion control are discussed for the following cases: (*a*) adsorption of a nonreducible (or nonoxidizable) substance; (*b*) reduction of an unadsorbed substance in presence of an adsorbed nonreducible substance; (*c*) reduction of an adsorbed substance. Treatments are given, whenever feasible, for electrolysis at constant potential, at constant current, and with superimposed alternating component. Experimental results and applications are described briefly.

Abstract No. 7

ANODIC OXIDATION OF VARIOUS METALS AT VERY LOW CURRENT DENSITIES

H. Johansen, G. B. Adams, Jr., and Pierre Van Rysselberghe

Recent research in the anodization of metals is briefly reviewed. Data concerning the anodic polarization of aluminum, titanium, hafnium, chromium, vanadium, niobium, and tantalum in ammonium borate solution for the range 0–100 μa current density are presented. Local currents for the free corrosion of the metals are estimated. A comparison of the formation rates of five of these metals is made on the basis of the Mott-Cabrera theory of metal oxidation.

Abstract No. 8

INHIBITION OF IRON CORROSION IN ACID SOLUTIONS*

Cecil V. King and Eric Rau

The inhibition of iron dissolution from rotating cylinders has been studied in solutions of dilute hydrochloric or perchloric acid with excess nitrate as depolarizer. No better oxidizing inhibitor than dichromate was found. Complexing and chelating agents greatly improve protection by dichromate in hydrochloric acid although they simultaneously shift the iron potential in the anodic direction. Iron is protected better by dichromate alone in perchloric acid; chelants tend to make the potential more cathodic, but shorten the time of protection.

* Work done under Office of Ordnance Research Contract No. DA-30-069-ORD-1113.

Neocupferron, which forms insoluble chelate salts with iron ions, protects iron for many hours in these solutions. Carbon monoxide was studied as an adsorption inhibitor.

Abstract No. 9

ELECTRICAL DOUBLE LAYER CAPACITY AND SURFACE AREAS OF METALS

Norman Hackerman and R. J. Brodd*

The relation between the polarization capacity of some metal electrodes, measured by a modification of the Bowden and Rideal method, and their surface area, measured in a specially constructed krypton adsorption unit, was investigated. The results are interpreted with the aid of the relationship between the work function of a metal and the potential of its electrocapillary maximum and the electrocapillary behavior of mercury.

* Present address: National Bureau of Standards, Washington 25, D. C.

Abstract No. 10

OXYGEN OVERVOLTAGE IN CONCENTRATED ACID SOLUTIONS

I. Perchloric Acid

T. R. Beck* and R. W. Moulton

Oxygen overvoltage was measured on platinum electrodes in 5M perchloric acid from −45° to +40°C and in 0.005-9M perchloric acid at 0°C. A limiting current density that was found is due to activation overvoltage at the anode surface. This limiting current density decreased at lower temperatures and in higher perchloric acid concentrations. It also marked the beginning of ozone formation. Adsorption of perchlorate ions is believed to be the cause of the limiting current density.

* Present address: Kaiser Aluminum & Chemical Corp., Permanente, Calif.

Abstract No. 11

INHIBITORY PROCESSES AT THE DROPPING MERCURY ELECTRODE

I. Structure of the Adsorbed Layer of Pyridine

L. Gierst* and D. Bermane

The surface excess of pyridine in alkaline solutions has been evaluated using electrocapillary measurements. The data obtained show that, after a critical amount of pyridine has been added, the quantity adsorbed becomes independent of further addition of pyridine and of the applied potential. These and other results lead to the conclusion that the adsorbed layer is monomolecular, close-packed, and oriented. A theoretical

* Present address: Faculté des Sciences, Université Libre de Bruxelles, Bruxelles, Belgium.

treatment is suggested to describe the properties of the organic adsorbed layer.

Abstract No. 12

INHIBITORY PROCESSES AT THE DROPPING MERCURY ELECTRODE

II. Inhibition of the Discharge of PbO_2H^- by Pyridine

L. Gierst* and D. Bermane

The influence of increasing quantities of pyridine on the discharge of PbO_2H^- in alkaline solutions has been studied using polarography and electrolysis simultaneously under constant current in unstirred solutions. From the kinetic data, the inhibition appears to proceed according to three different mechanisms, depending on the potential and the quantity of pyridine added. Results are consistent with the electrocapillary data, previously reported. Electrolysis under constant current in unstirred solutions is adequate to study the kinetics of irreversible reactions and permits, in particular, one to distinguish quantitatively between the several types of inhibitory processes.

* Present address: Faculté des Sciences, Université Libre de Bruxelles, Bruxelles, Belgium.

Abstract No. 13

RADIO-TRACER TECHNIQUE FOR CONTINUOUS MEASUREMENTS, IN SITU, OF ADSORPTION FROM SOLUTIONS

M. T. Simnad

An experimental technique has been developed to measure continuously the rates of adsorption of tagged ions from solutions on metal surfaces. The method can be used to study the rates of exchange, adsorption, and passivity. Preliminary results show that previous measurements of the activity of washed specimens are unreliable and are of qualitative value only, since variable amounts of the adsorbed layers are removed by washing. Theories based on such measurements are also of questionable value.

Abstract No. 14

KINETICS OF SILVER-SILVER ION EXCHANGE

C. V. King and Ann-Mari Simonsen

Silver exchanges rapidly with its ions on initial immersion in solution, with much slower exchange thereafter. In the present work, silver coupons were given repeated brief immersions in radio-silver nitrate solutions of four concentrations, with hot and cold water washing. The initial exchange was found to be of first order kinetically with one immersion as the time unit and maximum exchange corresponding to 35 to 50 atomic layers based on measured area. Measurement of the slow exchange indicates an exchange current density of 40×10^{-10} amp/cm² in 0.5*N* silver nitrate.

ELECTRIC INSULATION

Abstract No. 15

BIOLOGICAL INSULATING MATERIALS

R. N. Hazelwood

The properties and characteristics of electrical insulating materials in biological systems are reviewed. The function of lipids and lipoproteins in nerve conduction is discussed. Current work on the role of insulators in the photochemical reactions of photosynthesis will be described. Ultracentrifugal characterization of lipoproteins will be discussed.

Abstract No. 16

DIELECTRIC STRENGTH OF INSULATION SYSTEMS

D. A. Lupfer

(No abstract received)

Abstract No. 17

THERMAL EVALUATION OF INSULATION

E. L. Brancato

Advances in the evaluation of insulation systems are discussed and the present status of magnet wire, motorette, and motor aging studies is reported.

Abstract No. 18

THERMAL EXPANSION OF FILLED EPOXY RESINS

J. E. Carey

This paper discusses the importance of filler choice in formulating epoxy resins for encapsulation operations and presents some data on thermal coefficient of expansion vs. filler type and resin content.

Abstract No. 19

ELECTRICAL PROPERTIES OF SOME EPOXY RESINS

C. H. Klute

Epoxy resins are still relative newcomers to the field of electrical insulating materials. For this reason detailed information concerning their response to alternating current is not as readily available as is that for other common insulators. This paper is a report of progress of a continuing study of the electrical behavior of the EPON Resins manufactured by Shell Chemical Corp. The study is restricted at present to the low molecular weight species used in electrical casting compounds and will attempt to point out the electrical properties developed in the solid material when crosslinking is induced by each of three important types of amine catalysts, viz., amines with active amine hydrogen, tertiary amines, and amine salts.

Abstract No. 20

CHARACTERISTICS OF MULTILAYER DIELECTRICS

D. A. Lupfer

(No abstract received)

Abstract No. 21

APPLICATION OF INSULATORS AND WINDOW PROBLEMS IN VACUUM TUBES AT MICROWAVE FREQUENCIES

E. T. Jaynes

(No abstract received)

Abstract No. 22

EFFECT OF VOLTAGE AT ELEVATED TEMPERATURES ON INSULATION RESISTANCE OF CERAMIC CAPACITORS

K. H. Brandt

(No abstract received)

Abstract No. 23

MICROSTRUCTURE OF BARIUM TITANATES CERAMICS

I. E. Burkes and R. C. de Vries

(No abstract received)

Abstract No. 24

PHASE EQUILIBRIA AND SOLID-STATE REACTIONS IN THE SYSTEM OF TALC-CLAY

J. A. Pask

(No abstract received)

Abstract No. 25

ELECTROCHEMICAL ETCHING OF HIGH PURITY ALUMINUM CAPACITOR FOIL IN SODIUM CHLORIDE SOLUTIONS

G. H. Kissin and Gloria S. Murphy

The influence of electrolyte concentration, temperature, current density, and time was investigated for the anodic etching in sodium chloride solutions of 99.80, 99.87, and 99.99% aluminum foil. Metallographic examination and capacitance measurements of etched surfaces anodized in boric acid showed that the extent of etching and the configuration of the etched surfaces varied as the purity of the foil was changed. Optimum etching conditions for maximum increase in surface area were determined for application to the production of electrolytic capacitor anodes.

ELECTRONICS—LUMINESCENCE

Abstract No. 26

POTENTIALITIES AND DIFFICULTIES IN THE INTERPRETATION OF THE KINETICS OF LUMINESCENCE

M. Schön

(No abstract received)

Abstract No. 27

RADIATION RESULTING FROM THE RECOMBINATION OF HOLES AND ELECTRONS IN SILICON

J. R. Haynes

Radiation produced by the recombination of excess electrons and holes in silicon has been examined both at room temperature and at 77°K. The radiation obtained at room temperature is shown to be an intrinsic property of silicon. It is probably due to indirect transitions of electrons from the conduction band minima to the valence band with phonon cooperation. Additional radiation is found at 77°K which is structure sensitive. This radiation is shown to be produced by the recombination of excess carriers with un-ionized donor and acceptor impurities. Differences between the photon energies associated with the maximum photon emission of intrinsic and extrinsic radiation are in semiquantitative accord with accepted values of ionization energies of the donor and acceptor impurities introduced in the crystal growing process.

Abstract No. 28

PHYSICAL BASIS OF A MULTIPHONON PROCESS

J. J. Markham

Low temperature experiments in the alkali halide indicate that there must be a way for an electron to generate many phonons simultaneously when it drops from one state to another. A series of single phonon processes is believed to be too slow to explain the observations. The author attempts to give the physical basis of a multiphonon process by the use of Franck-Condon diagrams. This suggests why it should be a common phenomenon in solids.

Abstract No. 29

THERMOLUMINESCENCE OF MANGANESE-ACTIVATED CALCIUM FLUORIDE

R. J. Ginther and R. D. Kirk

The thermoluminescence of manganese-activated calcium fluoride has been investigated as a possible method for dosimetry of x-rays and gamma rays. It was found that samples containing from 1.0 to 5.0% Mn have a single glow peak at about 250°C. Samples of lower manganese concentration have low temperature emission peaks which render the dosage indication unstable through the thermal release of electrons from shallow traps. The presence of alkali impurities or of cerium shifts the thermoluminescence to lower temperatures, whereas concentrations of manganese above the optimum or the use of commercial materials in the synthesis result in poor efficiency.

Abstract No. 30

THERMOLUMINESCENCE OF TITANIUM-ACTIVATED LITHIUM SILICATES

P. J. Pizzolato

Thermoluminescent properties of titanium-activated lithium metasilicate phosphor make it of potential usefulness as a radiation dosimeter. This material has its main glow peak at 250°C and a smaller one at 90°C. Other titanium-activated lithium silicate systems, the disilicate and orthosilicate, were found to have lower sensitivities to gamma and x-radiation and less favorable glow curves. Initial work has shown a clearly measurable response to gamma ray doses as low as 10 roentgens (Co^{60}), a response nearly proportional to dose applied, stability of the high temperature glow peak on storage, and dose rate independence. These preparations were found to be energy independent in the range 100 kev to 1.2 mev, and the response to a given dose of 38 kev x-rays was five times that of an equivalent dose of 1.2 mev gamma rays.

Abstract No. 31

PREPARATION OF THE SELENIDES OF HYDROGEN AND ZINC

G. E. Crosby

The need for hydrogen and zinc selenide necessitated the study of various techniques for preparing these compounds. A report of a literature survey and a laboratory evaluation of many processes are given. Some processes are reported for preparing luminescent grade zinc selenide directly from selenium without use of the toxic hydrogen selenide.

Abstract No. 32

PREPARATION OF THE COPPER-ACTIVATED ZINC SELENIDE PHOSPHOR BY THE DRY PROCESS

G. E. Crosby

A dry process is described which yields the zinc selenide phosphor with luminescent properties equivalent to the same phosphor prepared from precipitated selenide. Optimum conditions for preparation and optimum chemical concentrations are discussed.

Abstract No. 33

ULTRAVIOLET FLUORESCENCE OF SOME TERNARY SILICATES ACTIVATED WITH LEAD

H. A. Klasens, A. H. Hoekstra, and A. P. M. Cox

The investigation of the phase diagrams of ternary systems containing SiO_2, one oxide of the group (CaO, SrO, BaO), and MgO or ZnO has led to the discovery of eleven new compounds some of which proved to be very good base materials for Pb-activated phosphors with emissions ranging from 3000 to 4000 Å. A suitable phosphor for "sun lamps" is $Ba(Zn, Mg)_2Si_2O_7$—Pb, for "black light lamps", $Sr_{0.6}Ba_{1.4}(Zn, Mg)Si_2O_7$—Pb.

Abstract No. 34

ALKALI COMPENSATED SILICATE PHOSPHOR

G. E. Crosby

Results of incorporating alkali ions into cerium-activated calcium magnesium silicate (Akermanite) phosphor are reported and discussed. Alkali ion compensation of the silicate phosphor yielded a product with greater luminescent efficiency and slightly shorter decay. Incorporation of alkali ion on preparation greatly improved the yield of good phosphor.

Abstract No. 35

AN AUTOMATIC RECORDING RADIOMETER

A. E. Martin, C. E. Meinheit,* and F. W. Harjes†

An automatic radiometer has been built for direct recording of excitation spectra of photoluminescent phosphors. Narrow bands of ultraviolet radiation provide the excitation. The central wave length of such bands lies within the limits 2200–4500 Å. The accuracy of the excitation efficiency is 5%. Another function readily provided is automatic recording of emission spectra of phosphors within the range 3300–6650 Å. The precision of recorded functions is approximately 1%. Absorption data can also be taken, although at reduced accuracy.

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† Present address: Sylvania Electric Products Inc., Kew Gardens, N. Y.

Abstract No. 36

SOME PRACTICAL ASPECTS OF ELECTROPHORETIC DEPOSITION

G. F. Kinney and J. V. Festa

Typical electrophoretic deposits employed in the electron tube industry are described with regard to suspension composition, equipment required, and nature of deposits obtained. The effect of added moisture and the effect of partial settling

also were investigated. It is pointed out that the three electrode processes, neutralization of charged particles, their deposition, and the electrode reaction, although occurring concurrently, can well occur independently.

Abstract No. 37

INFLUENCE OF CONVECTION AND OTHER FACTORS IN FLUORESCENT SCREEN UNIFORMITY

P. R. Myers and C. T. Lattimer

Television tube manufacture requires the application of screens with uniform weight-per-unit-area characteristics to provide a uniform screen color across the entire tube face. This paper covers an investigation of the effect of convection currents on screen weight uniformity from the theoretical and practical viewpoints. Studies of liquid movement by dye tracers and thermal gradients are presented along with screen application tests which culminated in screens of excellent weight uniformity through convection current assistance.

Abstract No. 38

TIME-AVERAGE ELECTROLUMINESCENCE OUTPUT OF SOME ZINC SULFIDE PHOSPHORS

Sol Nudelman and Frank Matossi

The dependence of time-average electroluminescence output on field strength and frequency is observed for frequencies up to 20 kcps for green and blue emission. Field dependence can be described either by a power law or by an exponential law. The frequency dependence is discussed in terms of theoretical relations (Curie) connecting the light output to recombination characteristics or to polarization effects. Light output from sinusoidal and square wave excitation is compared.

Abstract No. 39

ELECTROLUMINESCENCE OF ZINC SULFO-SELENIDE PHOSPHORS WITH COPPER ACTIVATORS AND HALIDE COACTIVATORS

I. J. Hegyi, S. Larach, and R. E. Shrader

Spectral distributions and emission intensities of Zn(S:Se):Cu phosphors will be discussed in detail. Both the color and intensity of emission are affected by the halide used as a coactivator. A decrease in the dominant wave length of emission is obtained in varying the coactivator from chloride to bromide to iodide. Higher intensity of emission is found when iodide is used as a coactivator in ZnS:Cu phosphors, and when bromide is used as a coactivator in Zn(S:Se):Cu phosphors. A red-emitting electroluminescent material will be described.

Abstract No. 40

PHYSICOCHEMICAL ASPECTS OF ELECTROLUMINESCENCE OF ZINC SULFIDE PHOSPHORS WITH COPPER ACTIVATOR

S. Larach, R. E. Shrader, and I. J. Hegyi

The role of the copper activator and of the halide flux in electroluminescent ZnS:Cu will be discussed from a physicochemical point of view. The effect of the flux on the amount of copper incorporated into ZnS will be described. Electroluminescence will be described in terms of a model which involves both copper and halide. Chemical barriers and other surface effects will be discussed.

Abstract No. 41

FURTHER EXPERIMENTS ON ELECTROLUMINESCENCE OF ZnS SINGLE CRYSTALS

D. R. Frankl

The major features of the light emission and current in electroluminescent ZnS crystals were discussed at the 1955 meeting. Refinements in technique have made possible the study of some of the less prominent features, including a small permanent polarization and several additional emission peaks. In addition, further studies of the dependence of the major emission peaks on voltage, waveform, and temperature have been made. These experimental results will be described and interpretations offered where possible.

Abstract No. 42

A THEORY OF THE ELECTROLUMINESCENCE OF ZnS SINGLE CRYSTALS

J. L. Birman

Field stabilization of traps and current excitation of centers, proposed as mechanisms involved in the electroluminescence of ZnS, have been tested on a model of a luminescent center consisting of three energy levels (ground, intermediate, and trap states) subject to periodic half-wave and d-c applied voltages. The results of the test, which will be discussed and compared with experiment, include the dependence of: (*a*) shape of the brightness wave; (*b*) magnitude of the brightness maxima; and (*c*) integrated brightness per cycle, on peak voltage, temperature, and frequency.

Abstract No. 43

SOME EXPERIMENTS ON PERSISTENT POLARIZATION AND PHOTOCONDUCTIVITY IN ZnS CRYSTALS

A. Lempicki

Certain ZnS synthetic crystals polarize under the influence of an electric field applied in the dark, and remain polarized for a long time after removal of the field. When the field is applied while the crystals are illuminated, polarization is much larger. High photocurrents can flow even when the crystal is polarized. Under illumination, polarization increases sublinearly and the photocurrents superlinearly with voltage. Shapes of photocurrent pulses under illumination of various wave lengths, and the effects of polarization thereon, are discussed.

Abstract No. 44

INCORPORATION OF CHLORIDE IN ZnS PHOSPHOR PREPARATION

A. Kremheller, A. K. Levine, and D. J. Bracco

Data are presented on recent investigations of the mechanism of the incorporation of chloride into zinc sulfide powders during firing. In continuation of previously reported work it is found that the temperature dependence of the retention of volume chloride in zinc sulfide is similar whether the flux is NaCl or $ZnCl_2$; the volume chloride shows a peak concentration near 500°C in both cases.

Abstract No. 45

THE RELEASE OF CHLORIDE FROM ZINC SULFIDE BY GRINDING

A. Kremheller and A. K. Levine

Grinding, followed by displacement washing, permits one to distinguish between lattice and internal surface chloride in ZnS powder fired with chloride flux. Data are presented on the amount of removable chloride for ball milling times up to 300 hr.

ELECTRONICS—SEMICONDUCTORS

Abstract No. 46

SURFACE STATES ON SEMICONDUCTORS

J. Bardeen

The following measurements have been used by various investigators to determine concentrations, energies, and trapping cross sections of surface states: (*a*) surface conductance and its variation with atmosphere and with applied external fields (field effect); (*b*) variation of conductance of an inversion layer with applied voltage (channel effect); (*c*) surface recombination; and (*d*) contact potential and change in contact potential with light. The present status of experimental results, mainly on germanium, and theoretical interpretation will be summarized.

Abstract No. 47

ELEMENTAL SEMICONDUCTORS

H. Y. Fan

Bulk properties of elemental semiconductors, germanium and silicon, will be

reviewed with emphasis on recent developments. Better knowledge of the energy band structure, energy gap, and effective mass has been obtained. Optical absorption photoconductivity and spin resonance are used to study impurity states and lattice imperfections. Interesting observations have been made and better understanding obtained for various conduction phenomena, including magnetoresistance, thermoelectric power, high field and low temperature conductivity. Much has been learned about carrier recombination and trapping.

Abstract No. 48

DEFECTS IN CRYSTALS OF SILICON AND GERMANIUM GROWN FROM THE MELT

E. Billig

Crystals of silicon and germanium have been grown from the melt under extreme conditions, and have been examined for crystal defects. Two specific types of defects could be introduced by varying growth conditions, and these were studied in great detail. Thin twin lamellae were produced by nucleation with a foreign impurity, while slip was produced by thermal stresses during crystal growth.

Abstract No. 49

RECTIFYING SEMICONDUCTOR CONTACTS

A Review of Theoretical Progress

H. K. Henisch

The purpose of this paper is to acquaint nonspecialists in this field with the present state of understanding of rectifying contacts between metals and semiconductors. The subject is reviewed with special reference to contacts whose behavior is controlled by electric charges in surface states. Methods are outlined whereby some of the relevant parameters can be measured and the reliability of these procedures is discussed. Other topics included in the survey are photoeffects, peak back turnover, and injection characteristics.

Abstract No. 50

DISTRIBUTION OF COPPER BETWEEN GERMANIUM AND TERNARY MELTS SATURATED WITH GERMANIUM

C. D. Thurmond and R. A. Logan

The solubility of copper in solid germanium has been measured as a function of the copper concentration in ternary Ge-Cu-Pb melts saturated with germanium at 700°C. Alloys of Ge-Cu-In, Ge-Cu-Sn, and Ge-Cu-Au have also been studied but to a more limited extent. The distribution coefficient of copper as a function of melt concentration is explained in terms of the expected interactions deduced from the binary phase diagrams.

Abstract No. 51

CONDUCTIVITY AND BAND GAP MEASUREMENTS OF SOME RELATIVES OF PHTHALOCYANINE

Wolfgang Felmayer and Irving Wolf

The electrical resistance of samples of powdered Cu-phthalocyanine, Pt-phthalocyanine, highly chlorinated Cu-phthalocyanine, and of two polymers of Cu-phthalocyanine were measured at various temperatures in a nitrogen atmosphere. All of the compounds showed semiconductive behavior. The highly chlorinated Cu-phthalocyanine and the Pt-phthalocyanine had approximately the same resistance as the Cu-phthalocyanine, whereas both polymers had lower resistances, one of the polymers having a resistance of about 10^{-3} that of Cu-phthalocyanine at various temperatures. Some theoretical implications of the above facts are mentioned.

Abstract No. 52

TERNARY COMPOUND SEMICONDUCTORS WITH THE CHALCOPYRITE STRUCTURE

I. G. Austin, C. H. L. Goodman, and A. E. S. Pengelly

Energy gaps have been measured optically for five semiconducting compounds of chalcopyrite structure (a triply substituted diamond-type lattice). Measurements of mobility, photoconductivity, and temperature coefficient of the energy gap have been made on some of them. Their preparation was difficult because of vapor pressure effects. There was also a tendency for crack formation, believed to be due to differential thermal expansion in the polycrystalline specimens.

Abstract No. 53

ELECTRONIC AND IONIC FLUCTUATION PROCESSES IN SEMICONDUCTORS

R. E. Burgess

The distribution of electrons between the conduction band, the valence band, and bound levels in a semiconductor exhibits: (*a*) spatial fluctuations due to unavoidable statistical inhomogeneity (chemical or physical) which are responsible for "patch" effects in semiconductor devices affecting particularly their reverse current and breakdown characteristics; and (*b*) temporal fluctuations which appear as noise and arise from the inevitable variations of the kinetics of electron-ion reactions about equilibrium. The theoretical foundations of these processes and a review of experimental data are presented.

Abstract No. 54

INFLUENCE OF THE ABSORPTION EDGES OF CADMIUM AND SILVER ON THE X-RAY DIFFRACTION PATTERN OF CADMIUM COMPOUNDS

R. J. Robinson and F. Schossberger

X-ray powder and rotation diagrams of hexagonal cadmium sulfide as obtained by Ni-filtered Cu K-OC radiation showed certain low angle lines and spots, respectively, which were tentatively explained by lattice imperfections or by the presence of an unknown modification. An analysis of the absorption conditions of the general radiation shows that the unique closeness of the absorption edges of cadmium (in the sample) and silver (in the film emulsion) could form a filter which selects a very narrow band of x-rays. The low angle diffraction phenomena then appear as Bragg reflections of hexagonal cadmium sulfide produced by an average wave length $\lambda = 0.475$ Å.

Abstract No. 55

THE STATUS OF SEMICONDUCTOR TECHNOLOGY

F. J. Biondi

(No abstract received)

Abstract No. 56

A METAL-SEMICONDUCTOR CAPACITOR

R. L. Taylor and H. E. Haring

A porous tantalum-tantalum oxide-manganese dioxide capacitor, which provides a far higher capacitance per unit of volume than can be obtained with any other capacitor heretofore available, will be described. Its size makes it extremely attractive for use in transistor circuits, and in other low voltage circuits requiring the ultimate in miniaturization. The construction, characteristics, and advantages of the new electronic device will be discussed.

Abstract No. 57

DESIGN OF DIFFUSED JUNCTION SILICON DIODES

H. S. Veloric and K. D. Smith

Development in the diffusion technology of silicon *p-n* junctions has made feasible a wide range of diffused junction silicon diodes with predictable breakdown characteristics. Units have been fabricated with breakdown voltages from 6 to 200 v and with areas from 100 square mils to 1 in.^{2} A number of process parameters such as the nature of the diffusant, oven time and temperature, and the type of starting material are considered in the device design. Characteristics of some illustrative fabricated devices will be presented and compared with design theory.

Abstract No. 58

SOME APPLICATIONS OF FIELD EFFECT STUDIES ON GERMANIUM SURFACES

E. N. Clarke

The field effect is time- and temperature-dependent and can be described by assuming that charge carriers are trapped in surface states. Recent results obtained in oxygen and in vacuum can be related to gas adsorption. Surface conduction induced by capacitively applied fields has proved useful in the study of excess currents on germanium *p-n* junctions. In particular, the work to be discussed will show how one might distinguish between ionic and electronic currents in the presence of water vapor.

Abstract No. 59

ANODIC OXIDATION OF SILICON

P. F. Schmidt

(No abstract received)

Abstract No. 60

ANODIC OXIDE FILMS ON GERMANIUM*

Solomon Zwerdling and Sumner Sheff

Thick oxide films have been grown on *n*- and *p*-type germanium by anodizing in an anhydrous NaAc-HAc electrolyte. The films showed uniform interference colors in white light. The microgram quantity of oxidized germanium in each was determined colorimetrically. From this and corresponding values of anodic current density, duration of electrolysis, and rate of increase of anode voltage, the current efficiency, differential formation field, and resistivity of the oxide were calculated. Several intervals of different growth rate were found during the course of an electrolysis.

* The research reported in this document was supported jointly by the Army, Navy, and Air Force under contract with Massachusetts Institute of Technology.

ELECTROTHERMICS AND METALLURGY—ARCS IN INERT ATMOSPHERES

CHARACTERISTICS OF HIGH CURRENT ARCS FOR CONSUMABLE ELECTRODE ARC MELTING

F. W. Wood and R. A. Beall

A study has been made of consumable electrode arcs including rates of burn-off of anode and cathode at various subatmospheric pressures, with particular application to titanium and zirconium arc melting furnaces. A formula is proposed to describe the variation of burn-off with pressure, some related factors are discussed, and results of similar studies are reviewed.

Abstract No. 62

ENERGY TRANSFER IN THE HIGH INTENSITY ARC

Lawrence Mead, Marilyn A. Marquis, Charles Sheer, and Samuel Korman

The mechanism whereby electrical input energy is transferred to electrode material in the high intensity arc is studied. Rapid vaporization of anode material is explained by abnormally high anode drop, effectively concentrating a major fraction of input energy on the electrode surface. A tentative explanation of subsequent superheating of anode vapor is given in terms of production and acceleration of ions in the fall space, followed by kinetic energy transfer from ions to neutral vapor.

Abstract No. 63

A DESCRIPTIVE STUDY OF CONSUMABLE ELECTRODE ARCS; THE PRESSURE DEPENDENCE OF THEIR MODE OF BURN-OFF —A FILM

F. W. Wood and R. A. Beall

Through the use of high-speed cinematography, a study was made of the mechanisms of metal transfer in consumable electrode arcs, and their variation with relation to the change of pressure of the surrounding atmosphere. Film strips show arcs between electrodes of titanium and of iodide process zirconium.

Abstract No. 64

EFFECTS OF MAGNETIC STIRRING ON TITANIUM INGOT QUALITY

D. E. Cooper and R. J. Krieger

In the consumable electrode arc melting process, use of a solenoid-type coil to induce stirring of the molten metal has been reported by various laboratories. This paper reports a study of the stirring effect in a laboratory size furnace producing double-melted titanium ingots of 9½ in. and 12-in. diameter.

The degree of stirring is dependent on the magnetic field intensity of the coil and the arc current. In this study a series of ingots was melted at two levels of arc current and varying degrees of magnetic field intensity. In general, it was found that an optimum degree of stirring produced the best as-cast surface (least amount of porosity). Even a small amount of stirring breaks up the large columnar grains normally associated with the as-cast ingot, and the higher degrees of stirring produce the shallowest molten pools. A compromise between these effects was found to produce better results than no stirring or by too high a degree of stirring.

Abstract No. 65

PROPERTIES OF THE ANODE FLAME OF THE HIGH INTENSITY ARC

Marilyn A. Marquis, Lawrence Mead, Samuel Korman, and Charles Sheer

A study is made of the thermal environment of material vaporized by the high intensity arc, with special emphasis on conditions prevailing in the anode tail flame. Using a steady-state approach, equations describing matter and energy balance of the anode flame are derived. Consequent effects of variation in power input, anode consumption rate, and ambient pressure on local temperature and matter density of the anode flame are examined and compared with experimental observations.

Abstract No. 66

CHARACTERISTICS OF CONSUMABLE ELECTRODE D-C ARCS IN ARGON

E. W. Johnson and G. T. Hahn*

Direct current arcs were struck in argon between horizontal electrodes of steel, titanium, molybdenum, tungsten, and graphite. The arc characteristics appeared to be determined primarily by the cathode material. With increasing cathode melting point the arcs became more stable and their heat distribution shifted markedly to favor the anode. These effects are apparent in color motion pictures of the respective arcs. The study is being extended to include arcs at reduced pressure.

* Present address: Massachusetts Institute of Technology, Cambridge, Mass.

Abstract No. 67

THE EFFECT OF VARIABLES ON THE MELTING RATE OF METALS IN THE CONSUMABLE ELECTRODE ARC FURNACE

W. H. Smith and R. M. Parke

The melting rates of metals in the consumable electrode arc process were determined as functions of the following variables: kind of metal, crucible to electrode size ratio, power input, melting pressure, and type of electrical circuit. Metals investigated were copper, iron, titanium, and molybdenum.

Abstract No. 68

THE HIGH INTENSITY ARC IN PROCESS CHEMISTRY

Charles Sheer and Samuel Korman

The high intensity arc, or "Beck" arc, well known to illumination engineers, presents interesting applications in chemical and metallurgical processes. Unique arc properties make possible rapid and efficient vaporization of electrodes. Refractory materials, as con-

sumable electrodes, can be vaporized, reacted in homogeneous phase, and condensed, without contacting furnace walls, at power consumptions of 4–7 kwh/lb. Applications to ore reduction in inert atmosphere and vacuum, halogenation, and other chemical reactions will be described.

Abstract No. 69

ARC MELTING IN A VACUUM

G. W. P. Rengstorff

Contrary to the general belief of a few years ago, metals can be arc melted in a good vacuum. Of course, the good vacuum (0.01 to 0.2 μ of mercury) is measured in the region above the arc. The arc itself is undoubtedly carried by metallic vapor from the electrode and the melt. This paper discusses some observations on the use of this metallic-vapor arc, particularly as applied to preparing high-purity molybdenum.

Abstract No. 70

VACUUM REMELTING OF SUPERALLOYS AND STEELS BY THE CONSUMABLE ELECTRODE PROCESS

W. W. Dyrkacz

Various properties of steels and superalloys remelted in vacuo by the consumable electrode process have been investigated. Electrodes used for remelting are air-melted, alloyed cast ingots of desired composition. Data will cover several superalloys, low alloy, tool, and stainless steels. A comparison will be made between air-melted and vacuum remelted materials in mechanical properties, gas contents, and cleanliness as determined by inclusion ratings and forged upset tests. A high-speed motion picture film showing the arc melting operation in a research-type furnace will be shown.

Abstract No. 71

ARC PROPERTIES IN THE FIVE RARE GASES

H. S. Morton* and R. M. Gage

High current arcs in the five rare gases have been studied. Voltage-current and voltage-arc length relationships are presented for currents from 50 to 400 amp DCSP, and for arc lengths of 0.025–1.0 in. A tungsten cathode with either a cold copper or a molten titanium anode was used. Calorimetric data are also given to show differences in heat dissipation to the anode and to the arc chamber.

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Abstract No. 72

A PILOT MODEL THREE-PHASE A-C CONSUMABLE-ELECTRODE ARC FURNACE

P. C. Magnusson, G. L. Schmidt, F. Caputo, and R. A. Beall

Considerable advantage can be shown through use of alternating current with regard to the capital investment in a power supply for controlled atmosphere arc melting. The furnace described here not only utilizes alternating current, but yields a billet shaped ingot, appropriate for rolling directly, omitting the billeting step. This is accomplished by placing the three consumable electrodes in line, and melting with the a-c power supply connected in wye. Discussion is given of the electrical characteristics, and the feasibility of up-scaling the design.

Abstract No. 73

A VACUUM ARC MELTING FURNACE FOR REFRACTORY METALS

O. Z. Rylski and H. V. Kinsey

An arc furnace for melting and alloying titanium and other metals in a protective atmosphere with continuous flushing at subatmospheric pressures is described. Some data on operational characteristics with different metals are presented.

The furnace is designed with the emphasis placed on adaptability to the diverse requirements of a research and development laboratory on a pilot-plant scale and can be used for consumable and nonconsumable electrode arc melting.

The exploratory results indicate high degree of soundness and good internal structure of metals arc-cast under reduced pressure and suggest a possibility of commercial application in such fields of metal industry where gaseous inclusions and reactive characteristics of metals are of importance.

Abstract No. 74

ELECTRODE CONTROL SYSTEMS FOR INERT ATMOSPHERE AND VACUUM FURNACES

E. J. Borreback

There are various types of regulators applicable to consumable or nonconsumable electrode control for inert atmosphere and vacuum melting furnaces. These types will differ mainly in the particular device employed to detect and relay the proper control message from the arc to the electrode positioning device. This paper discusses the operating characteristics and relative merits of various regulator types, listing them as mechanical, electromechanical, and electrical regulators. There is also some discussion regarding the ability of the regulator to overcome certain arc stabilizing deficiencies of the power supply.

Abstract No. 75

THE HIGH INTENSITY ARC: ELECTRODE REQUIREMENTS FOR METALLURGICAL APPLICATIONS

Samuel Korman and Charles Sheer

Vapor phase reactions by the high intensity arc involve rigid specifications for electrodes which comprise mixtures of carbon and nonconducting ore. Economic and reaction considerations on one hand and electrical requirements on the other impose conflicting specifications with regard to ore-carbon ratio. Vaporization rates vary linearly with current density, the slopes depending on latent and specific heats of particular components. Proper balance of factors is therefore essential to maximize erosion efficiency and yield.

ELECTROTHERMICS AND METALLURGY—MARGINAL ORES

Abstract No. 76

A NEW CONCEPT OF TREATING HIGH IRON BAUXITES IN THE ELECTRIC FURNACE

M. J. Udy

High iron bauxites and "red mud" wastes from the Bayer process are smelted without lime or basic fluxing material. Iron is reduced and removed as a very low titanium iron and the alumina and titanium oxide upgraded in a slag composed chiefly of Al_2O_3, SiO_2, and TiO_2. The slag is decomposable by sulfuric acid for the recovery of $Al_2(SO_4)_3$ and $Ti_2(SO_4)_3$ or as Al_2O_3 and TiO_2. The acid is recovered for re-use. Acid consumption is low because acid constituents of the slag are minor.

Abstract No. 77

UTILIZATION OF SILICEOUS MANGANESE ORES FOR PRODUCTION OF SILICOMANGANESE

W. E. Anable

Beneficiation and smelting studies by the Bureau of Mines have demonstrated effective methods for utilizing siliceous ores for the manufacture of silicomanganese. In pilot plant beneficiation test work, a high percentage of the manganese was recovered in the flotation concentrate that contained from 32 to 38% Mn and about 30% SiO_2 plus Al_2O_3. Reduction of the concentrate and off-grade manganese ores of comparable composition in the continuous electric smelting furnace resulted in the production of commercial silicomanganese.

Abstract No. 78

THE USE OF WASTE CARBONACEOUS MATERIALS IN ELECTRIC SMELTING

R. R. Rogers and G. E. Viens

Use of wood chips, bark, and other waste carbonaceous materials has been investigated in smelting experiments performed in a 250 kva arc furnace. The advantages and disadvantages of using such materials are outlined, particular attention being paid to results obtained in smelting a manganese ore. The importance of fixed carbon determinations is emphasized, and a new method for making such determinations is described. Data on the fixed carbon content and the bulk density of various waste carbonaceous materials are presented.

Abstract No. 79

ALASKA'S POWER RESOURCES IN RELATION TO MINERAL DEVELOPMENT

Ivan Bloch

A large number of potential Alaskan hydropower sites appear feasible of development. Some of them are favorably situated to facilitate the utilization of the Territory's mineral resources such as iron, copper, nickel, chromites, and possibly others. With decreasing availability of abundant, low-cost supplies of hydroelectricity in the 48 States, Alaska's power potential warrants immediate consideration, especially in the southeastern and central portions accessible to tidewater for electroprocess industry establishment.

Abstract No. 80

PRODUCTION OF THORIUM

T. C. Runion and F. L. Cuthbert

The role of thorium as a marginal raw material in our national economy is discussed briefly and the rudiments of the thorium production process are presented as developed by Iowa State College and as modified and improved by the National Lead Co. Reference is made to a wet process for making thorium tetrafluoride, to the induction melting of thorium in stabilized zirconia crucibles, and to the development of consumable electrode arc melting techniques for the production of high-purity thorium metal.

Abstract No. 81

PROBLEMS IN THE EXTRACTION OF THORIUM AND RARE EARTH FROM ORES

H. E. Kremers

Various types of domestic and foreign ores suitable for the production of thorium and rare earth materials are available. Industrial use of each type involves both chemical and economic problems. The relationships of costs of production, relative sizes of the markets for thorium and for rare earths, and degree of purification required determine the most suitable ore material.

Abstract No. 82

PROCESSING OF ALLUVIAL SANDS FOR THE RECOVERY OF TANTALUM-COLUMBIUM BEARING MINERALS

J. E. Shelton

This paper discusses the beneficiation of alluvial sands to concentrate selectively columbium-tantalum bearing minerals and other radioactive minerals as an aid in evaluating deposits and the production of commercial products. It describes the high ratio of concentration achieved by attrition scrubbing, magnetic, electrostatic, gravity, and flotation procedures.

Abstract No. 83

ELECTRODEPOSITION OF MOLYBDENUM

T. T. Campbell

A review of the literature on the electrodeposition of molybdenum from aqueous, nonaqueous, and fused salt systems is presented along with a discussion of work performed at the Albany Station of the U. S. Bureau of Mines.

This research was devoted principally toward attempts to electrodeposit molybdenum from nonaqueous media such as liquid ammonia, formamide, acetamide, hydrazine, and other organic solvents. While thin plates of pure molybdenum and various deposits of molybdenum alloys were obtained, the procurement of massive deposits of pure metal was not realized. In general, the work was confined to the halides of molybdenum and includes a discussion of the preparative techniques used in forming and handling the halides.

ELECTROTHERMICS AND METALLURGY—PYROMETALLURGICAL REFINING

Abstract No. 84

SEPARATION OF PLUTONIUM FROM URANIUM BY DISTILLATION, MAGNESIUM EXTRACTION, AND SALT EXTRACTION

R. A. Barney, A. G. Buyers, D. Cubicciotti, F. J. Keneshea, A. Saul, and S. J. Yosim

Experiments are reported in which plutonium is separated from uranium by pyrochemical processes. The methods described are: distillation, liquid metal extraction, and fused salt scrubbing. Scrubbing with molten UF_4 or a mixture of fluorides is very effective in removing Pu from uranium, while in the distillation method, the rate of evaporation of plutonium from uranium follows Raoult's law. Magnesium has been found to extract plutonium from uranium to a varying degree depending on the impurities present.

Abstract No. 85

PRECIPITATION PROCESSES FOR LIQUID METAL FUELS AND BREEDERS

R. J. Teitel

Uranium and thorium are very insoluble in liquid lead, bismuth, and tin at low temperatures. Consequently, practically all of the uranium or thorium in fuels and breeder systems, respectively, can be removed by precipitation of intermetallic compounds. The radiation products remain essentially in the liquid phase and can be removed by purifying the liquid phase after filtration or other phase separation processes. Data for this type of process are presented to illustrate the method along with flow sheets and some proposed physical arrangements.

Abstract No. 86

MELT REFINING OF URANIUM METAL

H. M. Feder, L. Burris, and N. Chellew

Minimum requirements for a method of recycling the fuel from a fast nuclear power reactor are: (*a*) repair of radiation-induced damage; (*b*) removal of deleterious fission products; and (*c*) conservation of bred plutonium. Data will be presented to show that melting and liquation of uranium in refractory oxide crucibles brings about the required purification by volatilization and preferential oxidation. The influence of operating conditions on the degree of refinement and on the recovery of uranium and plutonium will be discussed.

Abstract No. 87

URANIUM HEXAFLUORIDE DISTILLATION

R. K. Steunenberg

Various processing schemes have been proposed in which spent uranium fuels are dissolved in a liquid fluorinating agent such as bromine trifluoride. The uranium is recovered as the hexafluoride, which is purified and decontaminated from radioactive fission products by distillation. This concept has been extended to fuels such as zirconium and aluminum alloys, which are not attacked by bromine trifluoride. The fuel is dissolved by hydrofluorination in a high temperature fused fluoride medium, followed by volatilization of the uranium with gaseous fluorine or halogen fluorides. The radioactive fission product wastes are handled as small volumes of the solidified melt.

Abstract No. 88

URANIUM PURIFICATION BY ELECTROREFINING

L. W. Niedrach and A. C. Glamm*

The feasibility of a high temperature electrorefining process for the decontamination of uranium from associated fission products has been demonstrated. Use has been made of the low-melting alloys of uranium with nickel to obtain molten products at temperatures below the melting point of pure uranium. Decontamination factors of between 80 and 500 have been obtained for representative fission products. The effects of temperature, current, and salt-bath composition on cell efficiency and cell operation are discussed.

* Knolls Atomic Power Lab., operated by the U. S. Atomic Energy Commission by the General Electric Co.

Abstract No. 89

LIQUID METAL EXTRACTION OF REACTOR FUELS

A. F. Voigt, F. H. Spedding, A. H. Daane, and others

A number of metals, notably silver, rare earths, and alkaline earths, are immiscible with uranium in the molten state. Experiments have been conducted on the extraction of uranium, containing fission products, and plutonium, with silver and several rare earths. By a combination of volatilization and extraction, removal of plutonium and many of the fission products is obtained. The application of this technique to a simple decontamination and refabrication cycle for fuel elements will be discussed.

ELECTROTHERMICS AND METALLURGY—RARE EARTHS

Abstract No. 90

METALLURGY AND PHYSICAL PROPERTIES OF RARE EARTH METALS

F. H. Spedding

All of the pure rare earth metals have now been produced in appreciable quantities and the author will discuss the methods used to produce pure rare earth metals at Iowa State College, and the physical properties of these metals insofar as they have been measured.

Abstract No. 91

FLAME SPECTRA OF SOME RARE EARTHS

A. W. Berger and T. F. Powers

Flame spectra of some rare earths are presented. Quantitative analysis for scandium, yttrium, lanthanum, and lutetium in simple rare earth mixtures is rapid. Interference by rare earths of neighboring atomic numbers is considered and calibration curves given. The spectra were obtained in the hydrogen-oxygen flame using the Beckman DU spectrophotometer with flame- and energy-recording attachments.

Abstract No. 92

A CAUSTIC PROCESS FOR THE TREATMENT OF MONAZITE AND XENOTIME

Paul Kruesi

A process for the treatment of monazite, the principal ore of thorium and the rare earths, and xenotime, an ore analogous to monazite but containing principally yttrium group rare earths, is described. The process uses concentrated caustic soda solution at elevated temperature in primary treatment followed by separation of thorium and rare earths by selective solution with hydrochloric acid. Data relative to operating conditions, yields, and product purities in the industrial application of this process are presented.

Abstract No. 93

EQUILIBRIUM AND KINETIC STUDIES ON THE PRASEODYMIUM OXIDE SYSTEM

C. L. Sieglaff and L. Eyring

Equilibrium dissociation pressure studies, gravimetric analyses, and x-ray diffraction studies have been carried out on praseodymium oxides in the oxygen pressure range of 1–10 atm and a temperature interval of 200°–400°C. A phase diagram for the praseodymium oxide system is proposed for the several compounds, many nonstoichiometric, in the composition range $PrO_{1.8}$ to PrO_2. Kinetic studies have been carried out on the high pressure oxidation of $PrO_{1.833}$ to PrO_2.

Abstract No. 94

STUDIES ON COMPLEX FORMATION IN LANTHANON ALIPHATIC CARBOXYLATES

R. C. Vickery

The formation of complexes between the lanthanons and aliphatic carboxylic acids has been studied by various techniques. Stability constants have been derived for some of the complexes studied and these are seen to vary through homologous series according to the number of carboxyl ligands in the molecule. The presence of amino groups in the ligand molecule enhances complex stability. Correlation of absorption spectra with stability series and other data has been attempted and some degree of association has been found.

ELECTROTHERMICS AND METALLURGY—SUPER-REFRACTORIES

Abstract No. 95

HIGH TEMPERATURE MATERIAL REQUIREMENTS IN THE AIR FORCE

R. A. Jones

A general discussion will be presented of the problems presented by high temperatures in aircraft and aeronautical equipment. Complications resulting from aerodynamic heating will be discussed with emphasis on the role of heat resistant materials in surmounting these problems.

Abstract No. 96

RECENT NAVY EVALUATIONS OF CERAMIC AND CERMET MATERIALS

H. Hessing, J. J. Harwood, and J. F. Erthal

Recent naval activity in high temperature and stress resistant cermets and ceramics is briefly described. Navy Laboratory cross-bending (modulus of rupture), thermal-shock and creep-rupture tests on metal impregnated SiC and on hot pressed MoB_2, TiB_2, TiC, $MoSi_2$, B_4C and some combinations of these are reported. Hot spin evaluations of small integrally bladed cermet turbine wheels and industry development work for the Navy on boride cermets are also described. Tentative conclusions are indicated.

Abstract No. 97

DEFECT STRUCTURE AND THE TEMPERATURE DEPENDENCE OF STRENGTH OF AN INTERMETALLIC COMPOUND

J. H. Westbrook

The temperature dependence of hardness of the intermetallic compound AgMg was studied over the entire homogeneity range. The effect of defect structure on hardness at high homologous temperatures differs radically from that at low temperatures. These results, over virtually the full homologous temperature range, appear to rationalize previously contradictory studies of the effect of defect structure on the room temperature strength of intermetallic compounds.

Abstract No. 98

THE ELASTIC PROPERTIES OF SUPER-REFRACTORY MATERIALS BY A SONIC METHOD

S. M. Lang

In order to provide some of the engineering data necessary for the efficient use of various refractory oxides, carbides, borides, cermets, and intermetal-

lies, their elastic constants—Young's modulus, shear modulus, Poisson's ratio, and bulk modulus—have been determined at room temperature. Some data on the variation of these constants with temperature and oxidation have been obtained. Also, a statistical evaluation was used to correlate fabrication techniques and property values.

Abstract No. 99

KT SILICON CARBIDE

A New High-Density Silicon Carbide Body

K. M. Taylor

This paper describes a new, self-bonded silicon-carbide body having an average bulk density of about 95% of theoretical. Maximum impurities are approximately 5%. Strength at temperatures above 1400°C are much higher than for other silicon-carbide ware, except the hot-pressed form, which it resembles in structure. Other outstanding properties include impermeability, unusually high thermal conductivity, and excellent resistance to oxidation, erosion, and many corrosive materials. Unlike hot-pressed silicon carbide, it is readily fabricated into intricate shapes.

Abstract No. 100

INFILTRATED TITANIUM CARBIDE

An Improved Cermet for Turbine Bladings

C. G. Goetzel

Cermet-type materials based on titanium carbide suggest themselves for turbine bladings and nozzles because of their attractive stress rupture properties and lighter weight than that of conventional alloys. However, one of the major shortcomings of metal-bonded titanium carbide is its brittleness, inherent in all ceramics and cermets. The infiltration technique provides titanium carbide cermets with higher impact resistance and stress rupture properties than those of present blading alloys. Further, composite structures are produced containing binder alloy-rich leading and trailing edges and high-alloy root sections.

Abstract No. 101

THE EFFECT OF PARTICLE SIZE ON THE BULK DENSITY AND STRENGTH PROPERTIES OF URANIUM DIOXIDE SPECIMENS

M. D. Burdick and H. S. Parker

Fused uranium dioxide was separated into fractions of varying particle size by air separation. Specimens of the nominal size of ⅛ in. by ¼ in. by 1½ in. were formed by hydrostatic pressing, firing, and lapping. The interrelations between original particle size, flexural strength at several test temperatures, and bulk density are shown. Recrystallization of the urania fragments occurred during the firing treatment.

Abstract No. 102

SOME PHYSICAL PROPERTIES OF HIGH-DENSITY THORIUM DIOXIDE

S. M. Lang and F. P. Knudsen

A number of strength properties and the elastic constants of a very high density form of thorium dioxide were determined at both room temperature and at 1000°C. All of the test specimens attained at least 99% of theoretical density; all were extremely brittle. They were fabricated from a mixture of 99½% of low-calcined ThO_2 and ½% of CaO (by wt), hydrostatically pressed at 30,000 psi, and heated for 1 hr at 1800°C.

Abstract No. 103

"ROCKIDE" COATINGS FOR JET NOZZLES

W. L. Howe

(No abstract received)

Abstract No. 104

THE STATUS OF CARBIDES, BORIDES, CERMETS, AND INTERMETALLICS FOR HIGH TEMPERATURE SERVICE

M. F. Judkins

The need for a versatile high temperature material is evident—the problem is being attacked vigorously, but the solution is still in the future. Scant hope exists of finding a metal or developing a metallic alloy, if we discount the possibility of adequately protecting molybdenum. Carbides, borides, cermets, and intermetallics exhibit the greatest potential but their shortcomings compel serious design and service compromises. This presentation endeavors to interpret chemical, physical, and mechanical properties of existing material and to describe their fields of usefulness.

Abstract No. 105

USE OF CERMETS AS TURBINE BLADES

G. C. Deutsch

An investigation to determine the feasibility of utilizing cermets for turbine blading will be reviewed. Cermet blades were operated in a full-scale turbo-jet engine. It was found that problems arose in the mechanical blade fastening device, inspection for blade uniformity, and impact. Through design improvements in the fastening device and through improved inspections, lives in excess of 240 hr and greater reliability were achieved. Susceptibility to impact remains as an important problem area.

Abstract No. 106

USE OF SUPER-REFRACTORIES IN ROCKET THRUST CHAMBERS

W. R. Sheridan

The present paper deals with the use of super-refractories in rocket thrust chambers burning liquid propellants. The properties of an ideal refractory for this application are outlined, and results of tests on actual refractories are given. Materials included are silicon carbide, graphite, zirconia, zirconium boride, boron nitride, and several others. Finally, the field of potential application is suggested in terms of chamber size, duration of firing, and quantity to be produced.

INDUSTRIAL ELECTROLYTIC

Abstract No. 107

A COMMERCIAL PROCESS FOR ELECTROWINNING MANGANESE

M. C. Carosella and R. M. Fowler

A review of the development of a novel process for the electrowinning of manganese from aqueous solution is presented with emphasis on the raw materials used and the advantages gained thereby. As a result of the development of this process a commercial plant was built. A description of the method of quality control and chemical analyses and characteristics of the metal produced in the plant at Marietta, Ohio, is also given.

Abstract No. 108

CURRENT EFFICIENCY OF ANODIC OXIDE COATING FORMATION ON COMMERCIAL ALUMINUM ALLOYS

G. H. Kissin and R. V. Paulson

The current efficiency of anodic oxide formation in sulfuric acid of a number of commercially important aluminum alloys was studied. All alloys were anodized at a constant current density of 12 amp/ft² in 15% sulfuric acid at 25°C. Some exceptions were noted to the general rule that current efficiency varies inversely as alloy base purity. Contrary to previous reports in the literature, it was found that the anodic coating thickness obtained in a given anodizing time was independent of the alloy. Cell voltages observed in anodizing at constant current density bear no simple relationship to alloy composition. The behavior of several alloying constituents during anodizing was observed and an attempt is made to correlate this behavior with current efficiency and voltage data.

Abstract No. 109

THE STRUCTURE OF KANIGEN*

A. W. Goldenstein, G. Gutzeit,† W. Rostocker, and F. Schossberger

An analysis has been made of the structure of nickel deposit produced by the catalytic nickel generator process. X-ray and electron diffraction reveal that Kanigen is an amorphous solid. The structure appears to be unrelated to and independent of the nature of the substrate and of the thickness of the deposit.

Metallographic examination reveals a dense material free from voids and unusually perfect conformity to the substrate surface profile. Etching produced a lamellar structure. In platings the lamellae lie parallel to the plane of the substrate. Growth faults can be observed traversing the thickness dimension from substrate surface irregularities

* Trade name for the deposition product of a catalytic nickel generator.

† Present address: Associate Director of Research, General American Transport Corp., Chicago, Ill.

Abstract No. 110

STUDIES OF A VERTICAL ROTARY MERCURY CATHODE CELL

Shinzo Okada and Shiro Yoshizawa

Fundamental research and industrial tests on a vertical rotary mercury cathode cell in Japan will be reported, including studies of the mercury film formed on the rotary disk, characteristics of a small pilot cell, and then of an industrial-size unit. The latter was found to operate at a current efficiency and terminal voltage equivalent to the horizontal cell with the advantages of a smaller floor space and a higher purity of chlorine.

Abstract No. 111

ELECTROLYTIC PRODUCTION OF BROMATES

Takashi Osuga and Kiichiro Sugino

An electrolytic process for the production of potassium or sodium bromate using a pure lead peroxide anode has been operated successfully at Tokyo, by Sanwa Pure Chemicals Co. In this process, a concentrated bromate solution was electrolyzed continuously at a cathode of stainless steel at an anodic current density of 25 amp/dm² at 70°C; current efficiency—about 90%; anode consumption about 50–60 mg/K.amp hr. Pure crystalline bromate could be obtained by cooling the cell effluent at room temperature.

Abstract No. 112

(Scheduled paper withdrawn by author)

Abstract No. 113

POLARIZATION IN AN ALUMINUM REDUCTION CELL

W. E. Haupin

A method, combining the technique of current reversal with the use of an a-c bridge, is presented for determining electrolytic polarization in an aluminum reduction cell. Polarization was found to be composed of one part with a short time constant and another with a long time constant. Low anode baking temperatures, agitation, high alumina concentrations, or high NaF/AlF_3 ratios in the bath decreased polarization. Additions of MgF_2, CaF_2, or SrF_2 had no noticeable effect.

Abstract No. 114

RELATION OF CURRENT EFFICIENCY TO GAS COMPOSITION IN ALUMINUM REDUCTION CELLS

T. R. Beck

Data are presented to show that there are significant deviations from the Pearson and Waddington equation, per cent current efficiency = $50 + \frac{1}{2}(\%\ CO_2)$. The deviations are explained by formation of less than 100% CO_2 in the initial anode gas and/or secondary reaction of CO_2 with carbon and loss of equivalent aluminum without reacting with CO_2. An equation is derived for correlating the data and the parameters are discussed.

Abstract No. 115

ELECTROLYTIC PREPARATION OF THORIUM-BISMUTHIDE DISPERSIONS IN BISMUTH FOR BLANKET PREPARATION IN THE LMFR*

M. A. Steinberg, M. E. Sibert, and R. J. Teitel

In a liquid metal fuel reactor using thorium as the fuel material, such as the one under investigation at the Brookhaven National Laboratory, thorium is present in the form of Th_2Bi_5 dispersed in liquid bismuth. This thorium-bismuthide dispersion in liquid bismuth must be of such size and shape as to facilitate the pumping of the slurry in and out of the reactor for processing and through a heat exchanger for the extraction of heat for power.

Two methods of preparation have been investigated: electrolysis of $ThCl_4$ in alkali metal chloride melts using a liquid bismuth cathode and a similar method whereby fine crystalline thorium is first deposited on a solid cathode and then stirred into a bismuth pool beneath the salt bath. Dispersions of up to 25% Th have been prepared in the form of small (20–40 μ) equiaxed particles of Th_2Bi_5.

* This work was carried out for the Brookhaven National Laboratory, Associated Universities, Inc., Upton, N. Y., under Subcontract No. S-265, Contract AT-30-2-GEN-16-1.

Abstract No. 116

EVALUATION OF ELECTROLYTIC PARAMETERS IN THE PREPARATION OF THORIUM METAL BY FUSED SALT ELECTROLYSIS*

J. C. Bleiweiss, B. C. Raynes, and M. A. Steinberg

The preparation of thorium metal by the fused salt electrolysis of thorium chloride in molten sodium chloride under an inert atmosphere has been in part previously reported. The work now described entails an investigation of certain variables in the preparation of thorium metal by the electrolysis of thorium chloride in fused sodium and potassium chlorides. The parameters studied were the ratio of NaCl/KCl, the thorium ion content, the current density, and the electrolysis temperature. The effects of these variables on both the current efficiency and the physical characteristics of the cathode deposits obtained were ascertained. These parameters were substantiated in the scaling up of the process from a laboratory effort to a tenfold increase in operations.

* This work was carried out for the U. S. Atomic Energy Commission, Washington, D. C., under Contract AT-(30-1)-1335.

Abstract No. 117

THE MOBILITY OF THE IONS IN SILVER NITRATE-ALKALI NITRATE MIXTURES

F. R. Duke, Nobel Ida, and Boone Owens

The transport numbers of the ions in the pure salts, $NaNO_3$, KNO_3, $LiNO_3$, and $AgNO_3$, have been determined. In addition, the transport numbers in the three binary mixtures, $AgNO_3$-alkali nitrate, have been measured. The cations in each case carry the major portion of the current. The mobility of ions in these mixtures increases with decreasing concentration; that is, the minor constituent cation at each end of the composition scale has unusually high mobility. This phenomenon is discussed in terms of fused salt structure.

Abstract No. 118

THE MECHANISM OF TITANIUM PRODUCTION BY ELECTROLYSIS OF FUSED HALIDE BATHS CONTAINING TITANIUM SALTS

J. G. Wurm, Lucien Gravel, and R. J. A. Potvin

Titanium was produced by electrolyzing a molten bath of a sodium and potassium chloride mixture containing

potassium fluotitanate TiF_6K_2. The formation of trivalent titanium double fluorides of sodium and potassium always preceded the production of metallic titanium during the electrolysis. These new trivalent titanium compounds were positively identified as TiF_3,3KF and TiF_3,3NaF.

Definite proof was brought forward that during the electrolysis sodium is a primary product and that the mechanism involved in the production of titanium metal proceeds by secondary reactions in two steps: in the first step, the tetravalent titanium is reduced to the trivalent state; in the second step, the trivalent titanium is finally reduced to metallic titanium.

Abstract No. 119

THE ELECTROREFINING OF TITANIUM IN FUSED SALT MEDIA

D. H. Baker, Jr., and J. R. Nettle

A short review will be offered of the development of cells, the electrolyte, and factors pertaining to the recovery of high purity titanium by electrorefining of off-grade sponge and mill scrap. A description, with lantern slide sketches, of one prototype cell which has been developed will be given with a discussion of its operation and the actual mill cost for the electrorefining of scrap sponge.

Abstract No. 120

THE MECHANISM OF DEPOSITION OF TITANIUM COATINGS FROM FUSED SALT BATHS

M. E. Straumanis, S. T. Shih, and A. W. Schlechten

The mechanism of the titanizing process consists mainly (~96%) in the direct collision of titanium particles dispersed in a molten salt bath (KCl, NaCl, or mixtures) with the surface of submerged metallic or ceramic objects such as Si, Fe, steel, Cu, Ni, Co, Au, Pt, porcelain or "Alundum". The Ti particles stick to the surface and, if the temperature is high enough (for Fe above 910°C), the Ti diffuses into the substrate forming a diffusion layer, the thickness of which, depending on temperature and time, conforms with the diffusion equation of Rhines. Up to 4% of the coating may be produced by this mechanism. Coatings by this mechanism can also be obtained on Fe in baths of fused salts (KCl or NaCl) containing lower titanium chlorides rather than dispersed metallic titanium with the latter produced by the reaction

$2TiCl_2 + 3Fe = 3FeCl_2 + 2Ti$ or by the $TiCl_3$ disproportionation in reaction.

Abstract No. 121

DEPOSITION OF TITANIUM FROM TITANIUM-OXYGEN ALLOYS ON COPPER, IRON, AND MILD STEEL

S. T. Shih, M. E. Straumanis, and A. W. Schlechten

The presence of some oxygen was found to be beneficial in coating titanium on other metals in a fused alkali chloride bath. An improved method of titanizing was developed by controlling the amount of oxygen by the use of prepared titanium-oxygen alloys or of titanium fines of known oxygen content as a source of titanium. The coating occurred in helium for several hours at about 850°C in the case of copper objects, and 1000°C for those of iron and mild steel. The samples, even of intricate shape, were well coated on all sides. The coatings adhered well to the base metals and protected them from corrosion.

THEORETICAL ELECTROCHEMISTRY

Abstract No. 122

A STUDY OF THE CATHODIC REDUCTION OF OXIDE FILMS ON IRON

II. The Reduction of Magnetite

H. G. Oswin

The reduction of magnetite films on iron has been observed under anaerobic conditions. The effects of current density and various electrolytes are presented and discussed.

Abstract No. 123

MECHANISMS OF HYDROGEN PRODUCING REACTIONS ON PALLADIUM

II. Diffusion of Electrolytic Hydrogen through Palladium

Sigmund Schuldiner and J. P. Hoare

The rate of diffusion of hydrogen through several thicknesses of palladium for varying current densities was measured. The relationship between the diffusion current and the total polarizing current was established. The diffusion constant was calculated.

Abstract No. 124

MECHANISMS OF HYDROGEN PRODUCING REACTIONS ON PALLADIUM

III. Hydrogen Overvoltage on the Polarization and Diffusion Sides of a Cathode-Diaphragm

J. P. Hoare and Sigmund Schuldiner

Overvoltage-log current density relationships on both the polarization and diffusion sides of palladium cathode-diaphragms were measured. Effects of diaphragm thickness, cold working, and poisons were determined. It was shown that on the diffusion side, η_d is a concentration overvoltage and the rate of the hydrogen producing mechanism is diffusion-controlled.

Abstract No. 125

MECHANISMS OF HYDROGEN PRODUCING REACTIONS ON PALLADIUM

IV. Potential of the Alpha-Palladium/Hydrogen Electrode

Sigmund Schuldiner and J. P Hoare

In sulfuric acid solution it was shown that the equilibrium potential of an α-Pd/H_2 electrode against a Pt/H_2 electrode in the same solution was 50 mv positive. Although β-Pd is stable with respect to the alpha phase in the absence of solution, the reverse is true when the electrode is in contact with solution. A mechanism for the phase transition is proposed.

Abstract No. 126

COMPARISON OF THE VARIATIONS OF THE DIRECT METHOD OF MEASURING POLARIZATION

I. Potentiometric Study with Copper Electrodes in Acid Copper Sulfate Solution

A. L. Ferguson, L. O. Case, and R. S. Karpiuk

Three variations of the direct method were studied in detail depending on the position of the Luggin capillary tip of the reference half-cell: (*a*) the "front" method, (*b*) "back" method, and (*c*) the "hole" method. Because of the shape of the cell adopted, it was also convenient to compare the Haring method with the others. In this potentiometric study it was found that: (*a*) a uniform current density was absolutely necessary for significant results by any method of measuring polarization; (*b*) the back of the electrode must be insulated to limit the apparent surface area to the cross-sectional area of the cell; and (*c*) the corrections applied for the *IR* drop present in the front method are highly uncertain.

Abstract No. 127

COMPARISON OF THE VARIATIONS OF THE DIRECT METHOD OF MEASURING POLARIZATION

II. Oscillographic Study with Copper Electrodes in Acid Copper Sulfate Solution

A. L. Ferguson, L. O. Case, and R. S. Karpiuk

To determine whether the differences in polarization values obtained in the potentiometric study of the three varia-

tions of the direct method for measuring polarization were due to an active polarization, to an included IR drop, or to a combination of these components, the natural decay curves of the depolarization processes were studied with the aid of a cathode ray oscilloscope and auxiliary electronic apparatus. It was possible to identify and determine with a high degree of accuracy any IR drop present in the decay curves and to draw certain conclusions and recommendations for polarization measurements by the direct method.

Abstract No. 128

HYDROGEN OVERVOLTAGE ON LEAD

Edward Kure,* Ernest Yeager, and Frank Hovorka

Hydrogen overvoltage measurements on lead in sulfuric, hydrochloric, and nitric acids indicate Tafel slopes from 0.13 to 0.22, depending on the extent of anion adsorption and impurities. The formation of lead hydride and its subsequent decomposition in solution determine the upper limit for the linear range of the Tafel plots. This upper limit has been extended at least tenfold through the use of a flow system which discards the solution after it passes the cathode. In the presence of oxygen, the cathode potential is depressed to that of the lead-lead salt couple at currents below the limiting current density for the transport of oxygen.

* Electric Storage Battery Co. Fellow.

Abstract No. 129

HYDROGEN OVERVOLTAGE ON NICKEL*

Richard Jefferys, Ernest Yeager, and Frank Hovorka

Hydrogen overvoltage measurements have been made on nickel by the interrupter technique in sulfuric and hydrochloric acid solutions as a function of concentration and temperature. For 1N sulfuric acid at 25°C, the constants of the Tafel equation are $a = 0.43$, $b = 0.096$; for 1N hydrochloric, $a = 0.61$, $b = 0.11$. In both electrolytes, positive deviations from the Tafel equation occur at 10^{-2} amp/cm^2. These results are compared with hydrogen overvoltage measurements calculated from polarization data for simultaneous deposition of nickel and hydrogen from $NiCl_2$ and $NiSO_4$ solutions.

* Research partially supported by fellowship to R. Jefferys from Harshaw Chemical Co.

Abstract No. 130

MOLECULAR DESORPTION AS A RATE-DETERMINING STEP FOR HYDROGEN OVERVOLTAGE ON PLATINUM

Gerald Lozier,* Ernest Yeager, and Frank Hovorka

The desorption of molecular hydrogen is considered as a possible rate-determining step for hydrogen overvoltage on platinum as opposed to atomic recombination. Evidence including hydrogen overvoltage measurements on various platinum alloys is presented to support molecular desorption as rate-determining. For gold alloys of less than 85% mole fraction gold, the a and b constants of the Tafel equation are substantially the same as for pure platinum, while the limiting current density is approximately proportional to the mole fraction of gold.

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Abstract No. 131

NITROGEN OVERPOTENTIAL ON BRIGHT PLATINUM IN LIQUID AMMONIA SOLUTIONS

Morris Eisenberg

The polarization of bright platinum electrodes associated with the nitrogen evolution reaction (nitrogen overpotential) was determined in liquid ammonia solutions for the temperature range −38° to −65°C. Following corrections for concentration polarization, the results were interpreted as chemical polarization in the light of Tafel's equation. Values of the exchange current density, i_o, and of the transfer coefficient, α, were calculated and the results discussed in relation to the experimental conditions.

Abstract No. 132

HIGH CURRENT ELECTRONIC INTERRUPTER FOR THE STUDY OF ELECTRODE PROCESSES

W. E. Richeson and Morris Eisenberg

The design of a current interrupter capable of handling currents up to 5 amp and which can be modified to handle even larger currents is presented. The interrupter is exceptionally versatile, has a fast rise time, a variable conducting level, a switching rate of 500,000 cps to any longer period desired, allows symmetrical or asymmetrical switching, automatic or manual operation, and is capable of presenting a d-c level of current with any desired ripple placed on that level. Included are some experimental results to illustrate its application in studies of electrode polarization. Suggestions on how to avoid difficulties in the use of such a device, and a discussion of its design in relation to other interrupters are given.

Abstract No. 133

DIFFUSION-CONTROLLED METAL DEPOSITION ON STATIONARY MICROELECTRODES

T. Pavlopoulos and J. D. H. Strickland

The diffusion currents for the reduction of thallium, silver, lead, and cadmium ions at stationary platinum electrodes are shown not to conform to the Nernst diffusion equation but to an empirical equation $I_d = K.n.F.D^{3/4}.(C - C_e)^{1/2}.(1/2r + 1/\delta)$, where I_d is the current density, $(C - C_e)$ the concentration gradient at the electrode, r the radius of the electrode, and δ a transfer layer thickness. These results quantitatively support a treatment based on convective diffusion already suggested by Agar.

Abstract No. 134

PROBLEMS OF ELECTROCHEMICAL NOMENCLATURE AND DEFINITIONS

Pierre Van Rysseiberghe

The recent work of IUPAC and CITCE Commissions in the field of electrochemical nomenclature and definitions, and the present situation with respect to the following concepts: electromotive force, "electric tension," electrode potential, oxidation potential, reduction potential, redox potential, electrochemical affinity, oxidation affinity per Faraday, reduction affinity per Faraday, etc., are reviewed and discussed.

Abstract No. 135

MATHEMATICAL STUDIES ON GALVANIC CORROSION

V. Calculation of the Average Value of the Corrosion Current Parameter

J. T. Waber, John Morrissey, and John Ruth

Mathematical analysis for mean current density has been completed for one general and two limiting ratios of electrode and corrodent dimensions using the coplanar, juxtaposed arrangement of long, narrow electrodes as in previous papers. The mathematical expressions were reduced to numerical evaluations and the results summarized in perspective illustrations.

The characteristic ratio (λ/ℓ) was used to emphasize the fact that relative and not absolute dimensions of the system establish its behavior. Comparison between theory and two experimental studies shows good agreement.

Abstract No. 136

THE ANODE BEHAVIOR OF GERMANIUM IN AQUEOUS SOLUTIONS

D. R. Turner

Anode characteristics of *n*- and *p*-type germanium are different. A large voltage barrier is observed at about 0.8 ma/cm² current density at room temperature on *n*-type, but not on *p*-type electrodes. The barrier on 3 ohm-cm *n*-type germanium anodes breaks down at about 9 v in many electrolytes. During anodic dissolution, the surface appears to be covered with about a monolayer of oxide or hydroxide, suggesting formation of a complex ion with hydroxyl or oxide radicals attached. A mechanism is proposed for the over-all anode dissolution process.

Abstract No. 137

ELECTROKINETIC POTENTIALS ON BULK METALS BY STREAMING CURRENT MEASUREMENTS

II. Gold, Platinum, and Silver in Dilute Aqueous Electrolytes

R. M. Hurd and Norman Hackerman

The electrokinetic (ζ) potentials of platinum, gold, and silver were obtained from streaming current measurements in distilled water. The values were 60.8, 61.0, and 49.0 mv, respectively. The ζ potentials of these metals were also measured as a function of concentrations of KCl and KOH. Maxima were observed in all cases except that of gold in KCl solutions. These maxima are qualitatively related to the solubilities of the corresponding chlorides and hydroxides.

Abstract No. 138

ELECTROLYTES OF BINARY SOLUTES IN KETONES

J. E. Lilienfeld, Helen Y. Hsiao, and H. S. Myers*

In systems of a ketone, a phenolic compound, and sodium hydroxide, with conductivity as constant parameter, composition functions are referred to weight ratio of sodium hydroxide to phenolic compound as ordinates, and weight per cent of phenolic compound in ketone as abscissas. At about 30%, a minimum is common to the presented functions. This, and other findings, indicate an elementary functional dependence of conductivity on molecular weights of both organic components.

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Abstract No. 139

THE ALLOTROPIC MODIFICATIONS OF CALCIUM

J. F. Smith, O. N. Carlson, and R. W. Vest

X-ray diffraction patterns on calcium samples show that 99.9+% Ca exists in only two allotropic forms: face-centered cubic to 464°C and body-centered cubic above 464°C. These results differ from the widely accepted structure; handbooks and tables currently list the high temperature allotrope as hexagonal closest-packed. A previously reported intermediate allotrope of complex structure is due to contamination. The temperature dependence of the electrical resistivity of the 99.9+% Ca is linear for both the face-centered cubic and the body-centered cubic allotrope. Calcium was observed to be self-annealing at room temperature.

Abstract No. 140

A PROPOSED MECHANISM FOR THE ELECTROLYTIC CONDUCTANCE OF SODA-SILICA GLASSES

A. B. Rothman

The resistivity measurements of one group of experimenters gives the activation energy for the electrolytic conductance of soda-silica glass as a function of soda content. The activation energy was extrapolated to zero soda content from a least-squares fit of an assumed empirical relation. This energy, 31.1 kcal/mole, agrees well with another value, 31.2 kcal/mole, obtained from measurements on fused quartz using electrodes of sodium nitrite. A microscopic model for the mechanism of conductance is proposed and an expression for the activation energy is derived. The value at zero soda content from this relation, 30.7 kcal/mole, agrees well with the two values mentioned above.

Abstract No. 141

ELECTROCHEMICAL PROPERTIES OF A CATION-TRANSFER MEMBRANE

N. W. Rosenberg, J. H. B. George, and W. D. Potter

The electrochemical behavior of a cation-transfer membrane with respect to cations of various charge has been investigated. Measurements have been made of capacity, water content, Donnan sorption, conductance, water transfer, and transport numbers. The results suggest that ionic mobilities are lower in the membrane than in free solution and that there is a high degree of association between the cations and the charge centers of the membrane.

Abstract No. 142

ELECTROCHEMISTRY APPLIED TO ELECTROPHYSIOLOGY

R. H. Beutner

Electrochemistry knows two types of potential differences: (*a*) those occurring by contact of aqueous solutions, either with metallic electrodes, or with water-immiscible electrolytic conductors (e.g., massive, fused AgCl can replace metallic Ag in Nernst's concentration cell); these p.d.'s, neglected in electrophysiology, are unrelated to ionic mobility; (*b*) "diffusion potentials" occurring between miscible solutions. These depend on ionic mobility. Electrophysiology relies on this type exclusively and uses the unproven hypothesis that ions acquire differential mobility inside membranes.

FALL MEETING

at the

STATLER HOTEL

Cleveland, Ohio

September 30, October 1, 2, 3, and 4, 1956

Sessions will be scheduled on

Batteries

Corrosion

Electrodeposition

Electrothermics and Metallurgy

Theoretical Electrochemistry (joint symposium with Electrodeposition)

Abstracts for the Fall Meeting (*not exceeding 75 words in length*) must reach the Secretary's Office, 216 West 102nd Street, New York 25, N. Y. *not later than June 15, 1956* in order to be included in the program.

Indicate on abstract for which Division's symposium the paper is to be scheduled.

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NOTE

Hotel reservation cards for the Hotel Mark Hopkins will be mailed to members of the Society about March 15.

Separate program booklets will *not* be mailed to members. Reprints of the above program in booklet size will be available at the meeting.

Post-Convention Trips

Two special post-convention trips have been worked out and will be offered to members and guests attending the Society convention in San Francisco. One of these tours will go to Yosemite National Park, the other to the Monterey Peninsula and vicinity. Reservation blanks and folders will be mailed the latter part of February to Society members residing in the U. S. and Canada.

Nonmembers, and members living outside the U. S. and Canada, who expect to attend the convention and are interested in taking one of the tours should contact Mr. T. H. May, California Parlor Tours Co., 371 Market St., San Francisco 5, Calif., mentioning The Electrochemical Society trips, or make arrangements through their travel agents. There probably will be a deadline of April 1 for the Yosemite trip, in view of the limited accommodations in the Park.

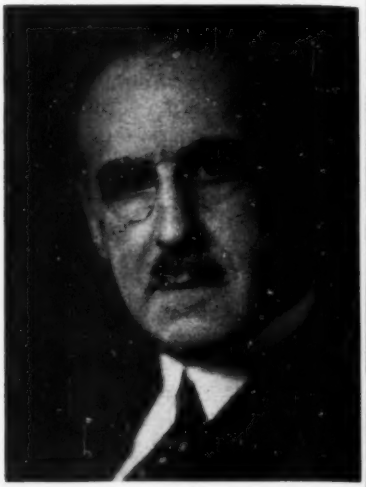
DECEMBER 1956 DISCUSSION SECTION

A Discussion Section, covering papers published in the January–June 1956 JOURNALS, is scheduled for publication in the December 1956 issue. Any discussion which did not reach the Editor in time for inclusion in the June 1956 Discussion Section will be included in the December 1956 issue. Those who plan to contribute remarks for this Discussion Section should submit their comments or questions in triplicate to the Managing Editor of the JOURNAL, 216 W. 102nd St., New York 25, N. Y., *not later than September 1, 1956*. All discussions will be forwarded to the author, or authors, for reply before being printed in the JOURNAL.

Current Affairs

Electrochemical Society Establishes F. M. Becket Memorial Award

H. B. Linford (*left*), professor of chemical engineering at Columbia University and Secretary of The Electrochemical Society, accepts a check for $10,000 from A. L. Foscue, President of the Electro Metallurgical Co., to establish the F. M. Becket Memorial Award. Mrs. E. B. Folwell, of Greenwich, Conn., daughter of Dr. Becket, witnesses the presentation.



F. M. Becket

As a fitting tribute to the pioneering achievements of Dr. Frederick M. Becket in the field of metallurgy, The Electrochemical Society has established the F. M. Becket Memorial Award. The award, in the form of an annual scholarship, is aimed at interesting college students in the field of high temperature electric furnace operations.

The fund for the award was presented to the Society by the Electro Metallurgical Co., a Division of Union Carbide and Carbon Corp. It is a cooperative effort to help alleviate the critical shortage of scientific personnel in the highly specialized field of metallurgy in the process industries.

Second or third year students working toward a Bachelor of Science degree will have the opportunity to qualify for the award by completing a special project. The project will be chosen by a board of experts from industry and education and will be so selected that the student's ability and originality in the field of electrothermics can be evaluated. Such projects may include construction of a scale model commercial unit, design of equipment, construction of a flow sheet for a commercial process, or a technical thesis. The scholarship to be awarded each year will be approximately $500.

Dr. Becket graduated from McGill University with a Bachelor of Science degree in 1895 and received a Master of Arts degree from Columbia University in 1902. He was one of the founders of the Niagara Research Labs. which operated in Niagara Falls from 1903 to 1906. He joined the Electro Metallurgical Co. and Union Carbide Co. in 1906, subsequently becoming President of the Union Carbide and Carbon Research Labs. and Vice-President of Union Carbide Co., Electro Metallurgical Co., and Haynes Stellite Co.

Dr. Becket was a pioneer in the production of low-carbon ferroalloys and was the inventor of most of the silicon reduction methods now employed. He was the first producer of ferrovanadium and low-carbon ferrochrome in America. Besides his work in the production of ferroalloys, he made many contributions to the art of ore dressing and to the metallurgy of steel alloys. Approximately 125 United States patents covering many fields were awarded to him.

Dr. Becket was honored for his achievements by the award of the Perkin Medal of the Society of Chemical Industry in 1924, the Acheson Medal of The Electrochemical Society in 1937, the Cresson Medal of the American Institute of Mining and Metallurgical Engineers in 1940, and honorary degrees of Doctor of Science from Columbia and Doctor of Laws from McGill University. He served as President of The Electrochemical Society and the American Institute of Mining and Metallurgical Engineers.

The Electrothermics and Metallurgy Division of The Electrochemical Society, which administers the award, deals with high temperature processes which require uses of electrical energy as a means of producing heat. The Division is particularly interested in electric furnacing by electric arc, resistance, or high-frequency means. It is also interested in the production of calcium carbide, ferroalloys, graphite, abrasives, and phosphorus, as well as other metals and alloys.

The original draft of the award was prepared by a committee consisting of Arthur C. Haskell, Titanium Alloy Manufacturing Division, who is Electrothermics and Metallurgy Division Chairman; G. M. Butler, Carborundum Co., E. & M. Division Vice-Chairman; and Arthur T. Hinckley, Oldbury Electro Chemical Co.

The committee was later enlarged to include Marvin J. Udy, well-known Niagara Falls consultant and Past

President of the Society, and Joseph H. Brennan, Electro Metallurgical Co., under the chairmanship of Ivor E. Campbell, Battelle Memorial Institute, who originated the idea.

After all details of the award had been settled, the Electro Metallurgical Co. willingly agreed to provide the funds necessary to finance the award.

The Board of Directors of The Electrochemical Society wishes to express its appreciation for the grant of $10,000 from the Electro Metallurgical Co. establishing the F. M. Becket Memorial Award. This grant will aid the Society in carrying out its educational program and will stimulate able young men to enter the field of electrochemistry and, in particular, the branch of electrothermics.

News Notes in the Electrochemical Field

Hackerman and Fontana to Receive 1956 NACE Awards

Two Electrochemical Society members with a long record of activity in corrosion mitigation have been selected to receive the 1956 Awards of the National Association of Corrosion Engineers. The 1956 Whitney Award will go to Norman Hackerman, professor of chemistry at the University of Texas in Austin, and the 1956 Speller Award to Mars G. Fontana, professor of metallurgical engineering at Ohio State University, Columbus. Presentation of the awards will be made at the annual banquet to be held at the Hotel Statler, New York City, during the March 12–16 NACE 12th Annual Conference.

Both honorees have been members of NACE since 1946. Dr. Fontana was NACE President 1952–53, and Chairman of the NACE Technical Practices Committee 1950–51. Dr. Hackerman has been active as a member of the board of directors and as Chairman of the NACE Education Committee, and organized and conducted the 1949 University of Texas-NACE Short Course on Corrosion.

Dr. Fontana, in addition to being professor of metallurgical research at the Engineering Experiment Station at Ohio State University, is a consultant for several metallurgical companies. He is the author and coauthor of numerous articles.

Dr. Hackerman, who joined the staff of the University of Texas in 1945, at present is professor of chemistry and chairman of the department, and director of the Corrosion Research Lab. He is First Vice-President of The Electrochemical Society and is Technical Editor of the Society's JOURNAL, a post he has held since 1950.

National Science Board Elections

Detlev W. Bronk, President of the Rockefeller Institute for Medical Research, New York City, is the newly elected Chairman of the National Science Board, governing body of the National Science Foundation. The election of Bronk by the Board was announced by Alan T. Waterman, Director of the Foundation. Dr. Bronk succeeds Chester I. Barnard, whose term as Chairman had expired.

Also announced was the election of Paul M. Gross, Vice-President and Dean of Duke University, Durham, N. C., as Vice-Chairman of the Board and Chairman of the Executive Committee.

NACE 1956 Corrosion Conference

Corrosion problems in industries and what is being done to solve them will be stressed in the technical program of the National Association of Corrosion Engineers 12th Annual Corrosion Conference. The conference will be held concurrently with the 1956 Corrosion Show, March 12–16, at the Hotel Statler, New York City. Symposia and discussion groups aim to provide maximum information in minimum time. Plans developed thus far include symposia on: Atomic Energy, High Temperature Corrosion, Chemical and Process Industries, Refinery and Oil and Gas Production, Metals and Plastics, Pipe Line Corrosion, Power and Communications, General Subjects. The four-day conference will end Friday, March 16, with a General Corrosion Round Table devoted to informal discussion by the audience of questions or problems submitted either by mail or from the floor.

Four technical papers from foreign sources have been accepted for presentation during the NACE Conference. At least two other papers are in the negotiation stage. W. Z. Friend, International Nickel Co., Inc., chairman of the technical program committee, has issued the following information about these papers:

Corrosion by Low-Pressure Geothermal Steam by T. Marshall and A. J. Jughill, Dominion Lab., Dept. of Scientific and Industrial Research, Wellington, New Zealand. Cathodic Protection of Creole Petroleum's Lake Maracaibo Gathering System by R. L. Benedict, Creole Petroleum Corp., Cabimas, Edo Zulia, Venezuela, S. A Cathodic Protection of Ship Hulls, Large Farm Water Piping, Domestic Water Boilers, Deep Well Pumps, and Concrete-Lined Prestressed Steel Water Conduits by D. Spector, Tel Aviv, Israel. Concerning Naphthenic Acid Corrosion by someone connected with N. V. de Bataafsche Petro Maatschappij, The Netherlands. Two papers are in negotiation through the offices of the Inter Society Corrosion Committee from authors in Germany and Italy. Titles given are not necessarily those which will apply to the final version of the papers.

Conference on Marine Corrosion and Fouling Problems

The University of California Extension through its division in the Department of Engineering has announced plans for a Conference on Marine Corrosion and Fouling Problems to be held April 18, 19, and 20 on the La Jolla campus of the University. The purpose of the conference will be to present the latest developments and thought on marine corrosion problems in a series of papers by recognized authorities. It will provide a forum for discussion of measures for protection against biological, physical, and chemical deterioration of wood, metal, and concrete structures in a marine environment.

Major topics during the conference session in the Library Building of the University's Scripps Institution of Oceanography will be: Introduction to the Study of Deterioration; Fundamental Causes of Deterioration; Deterioration Investigation; and Deterioration Mitigation Procedures. Chairman of the program committee is Claude E. ZoBel, professor of microbiology at the University. Cooperating with the university is the National Association of Corrosion Engineers. General Chairman of the conference is Charles D. Wheelock of the Institute of Marine Resources at the University in La Jolla.

Registration forms and information concerning the La Jolla conference are

available on request to: University of California Engineering Extension, Los Angeles 24, Calif. Fee for the three-day event is $25.00.

J. H. Hildebrand's Views on White House Conference

The United States may easily become "a subject nation" if it cannot do more than the White House Conference on Education did late in 1955 to achieve "schooling adapted to a world situation which calls for our utmost in trained intelligence and moral fiber."

This warning was sounded by Dr. Joel H. Hildebrand, President of the American Chemical Society and its delegate to the conference, in a statement made public recently. Professor Hildebrand, a member of the University of California faculty for more than 40 years, criticized in particular the failure of the conference to give adequate attention to the "catastrophic decline in many schools in enrollments and teaching competence in science and mathematics, subjects now basic to the very survival of Western civilization."

He asserted that there was no chance of getting into the final conference report anything seriously critical of "certain doctrines and practices largely responsible for the present deplorable and dangerous situation."

At every stage in the discussion, Dr. Hildebrand said, "there were watchful men who honestly believe more in 'social competency' than in grammar and arithmetic," who helped ward off criticism of existing school doctrines and practices. About one-third of the delegates, he estimated, were professional educators—"that is, superintendents, principals, and professors of education, not teachers."

To illustrate the difficulty of getting any criticism of current school policies into the conference report, Dr. Hildebrand cited certain experiences of delegates at his table—Table 40, one of 180 tables of delegates. For one thing, they took a stand against setting up for the schools too many objectives that "are either relatively unimportant or beyond their capacity to attain." The report on objectives not only ignored this principle, but on the contrary offered "fourteen points," with no analysis of their relative importance or practicability.

On the question "How can we get and keep good teachers?" the following statement was adopted by Table 40:

"There are many persons well qualified to teach, by virtue of intelligence, knowledge of specific subjects, facility in speech, personality, and sympathetic understanding of young people, who could be recruited to teach school if these natural qualifications were accepted for certification in place of course requirements in education.

"Many persons, otherwise well qualified, are repelled by courses in education that they regard as repetitive, doctrinaire, or inferior in intellectual quality."

This Dr. Hildebrand described as another trial balloon which was shot down as he expected. The requirement of 18 or more units of education for certification as a "qualified" teacher, and then of summer session credits in education for the teacher who aspires to salary increases, "provides positions for a vast number of professors of education—jobs that they, of course, do not intend to see jeopardized," according to Dr. Hildebrand, who commented: "That is part of the cost of education we are all expected to bear."

These professors, he emphasized, "are not wicked men—they honestly believe in the doctrines they teach."

"The procedure followed in this conference," Dr. Hildebrand continued, "represented, first, a sincere attempt to arouse more public interest in the welfare of the schools, in which respect it has commendably succeeded, and second, to obtain 'grass roots' opinions, for which I think it was poorly planned. The procedures were too much like those that the Soviets call 'democratic,' where opinions may be expressed more or less freely at the bottom level, but in their ascent to higher levels they are worked over and over by good party men, and finally emerge as orthodox 'party line.'

"The democratic way is very different. To begin with, the questions are formulated, not by quasi-neutral committees, but by keen-minded eager partisans of opposing views. They are then debated in the open, in press, in radio, and on platforms. The public listens, argues, writes letters to the papers, and all finally vote, either directly or indirectly. An attack upon the school problem in that way would not have brought forth 'fourteen points,' with no analysis of their relative importance, where subjects like chemistry or grammar, that can be *taught*, are confused with 'attitudes,' such as 'respect and appreciation for human values . . .' that can be *caught* by association with those who have them, but not *taught*.

"In place of the complacent statement that 'the schools are doing the best job in their history in teaching these skills,' it might have been possible to arouse among the participants some of the true, but unperceived, implications of the fourteenth point, 'An awareness of our relationships to the world community.'

"Our relation to the world community may easily become that of a subject nation if we can do no better than we did in this White House Conference to achieve schooling adapted to a world situation which calls for our utmost in trained intelligence and moral fiber."

Titanium Sponge Plant

Construction of the first titanium sponge plant in the United States utilizing the sodium reduction process is proceeding rapidly at Ashtabula, Ohio. For a year construction crews have been transforming the 100-acre site into the new plant which will mark the entry of the Electro Metallurgical Co., a Division of Union Carbide and Carbon Corp., into titanium sponge production. When completed, the plant will produce 7500 tons of titanium sponge per year. Electromet's process was developed in the company's Metals Research Labs and produces titanium sponge by reducing titanium tetrachloride with sodium. Production is expected to start in the third quarter of 1956.

Research Fellowships

The International Business Machines Corp. has announced that it will award industrial research fellowships to enable recipients to continue their academic research programs beyond the doctoral level. The grants will be made annually by a special awards committee headed by Dr. Arthur L. Samuel, research advisor at IBM, and assisted by an advisory panel of scientists and educators. The program will support significant research which might not otherwise be undertaken and, although projects need not have direct bearing on IBM's development program, preference will be given to proposals which fall within the company's broad range of interest and can be continued without difficulty in IBM research laboratories.

Graduate students at four universities have each received a $1500 Sylvania Fellowship to support studies in advanced electronics, solid-state chemistry and physics, and electrical engineering for the 1955–56 college year, it has been announced by Max F. Balcom, Board Chairman of the Sylvania Foundation, which administers the fellowship fund. Recipients of the 1955–56 Sylvania Fellowships are:

Daniel G. Dow of Dayton, Ohio, who is studying microwave electronics at Stanford University, Stanford, Calif., under Professor Dean Watkins.

Robert Mazelsky of Freeport, N. Y., who is studying silicates of the transition metals with unusual oxidation states at the University of Connecticut, Storrs, under Professor Roland Ward.

A. S. Miller of Danville, Ill., who is studying imperfections in solid silver bromide, using conductivity and diffusion techniques, at the University of Illinois, Urbana, under Professors G. M. Almy and Frederick Seitz.

Robert J. Martin of Pleasant Ridge, Mich., who is studying Townsend currents at the University of Michigan, Ann Arbor, under Professor W. G. Dow.

RCA Electrofax Process for Making Printing Plates

A new method of preparing offset and photoengraving printing plates, involving a single photographic operation thousands of times faster than conventional methods, was described on December 8, 1955 by Harold G. Greig, Radio Corp. of America, at the meeting of the Rochester Section, Photographic Society of America.

The new process employs the RCA Electrofax system of electrostatic photography. Mr. Greig stated that it makes possible the production of a complete lithographic plate in less than a minute, and reduces to a few minutes the time required to prepare a printing plate for etching. In addition, he described application of the process to the swift production of printed circuits for use in electronic devices.

The RCA Electrofax system, developed at the David Sarnoff Research Center of RCA at Princeton, N. J., is a new method of producing images or printed characters on any paper, wood, metal, plastic, or other surface coated with an inexpensive photoconductive pigment.

Perkin-Elmer Acquires Warren Electronics

The acquisition of Warren Electronics, Inc., specialists in ultraviolet spectroscopy, by The Perkin-Elmer Corp. was announced recently by Richard S. Perkin, President and Chairman of the Board.

Warren Electronics was formed in 1951 by Charles W. Warren as a development company providing electronic and instrument consulting capacity to the chemical industry. The firm is best known for the Spectracord, a fully automatic, high-speed ultraviolet recorder. For the present, Warren Electronics will continue operations in its Bound Brook, N. J., plant as a subsidiary of Perkin-Elmer, with Mr. Warren remaining as President.

Electron Tube Information Service

The National Bureau of Standards has established a tube information service for accumulating and disseminating technical data on both domestic and foreign radio tubes. At the present time nearly 10,000 cards, filed by tube type number, are appropriately referenced to manufacturers' source material. In addition, about 10% of these cards, selected mainly from the high-use miniature and subminiature types, have been coded on punched cards for mechanical sorting.

With this unique service, it is possible to find (*a*) information about any particular tube; (*b*) all tube types whose electrical characteristics, bulb sizes, or base configurations fall within particular ranges; and (*c*) domestic tubes that can be substituted for unavailable foreign tubes. Recently, junction diodes and transistors have been added to the Bureau's program. The program began about seven years ago as a service to NBS personnel. It has since been extended to all scientists and engineers in Government and industry who have legitimate requests. This continuing service is being carried out by C. P. Marsden and J. M. Moffitt of the Bureau's electron tube laboratory.

New Simpson Representative

The Simpson Electric Co., Chicago, Ill., has announced that E. A. Dickinson & Associates, 744 No. 4th St., Milwaukee 3, Wis., have joined Simpson to act as representatives covering the territory of the state of Wisconsin except for the portion west of Alma, Wis., on a straight line north to Superior.

Automatic Lead Cladding Machine

The rapid expansion of the nuclear industries has resulted in a large demand for metal products with the strength of steel and the shielding properties of lead, according to Alfred P. Knapp, president of Knapp Mills, Inc. of New York.

Six patent applications have been granted to the American Viscose Corp. and Knapp Mills, Inc., covering an automatic lead cladding machine which creates a homogenous bond between steel and lead, giving the finished product the desired strength plus the ability to shield against the escape of harmful rays from nuclear reactors. The new automatic cladder will make hand-made lead clad steel production far quicker and more efficient.

Solvay's 75th Anniversary

Solvay Process Div., Allied Chemical & Dye Corp., enters its 75th year of chemical manufacturing in 1956 with construction of its new hydrogen peroxide plant at Syracuse, N. Y., completed and with work on its new chlorine-caustic soda facilities at Brunswick, Ga., well under way.

The hydrogen peroxide installation, which utilizes a new manufacturing process, is situated near the site of one of America's first chemical centers. It was at Syracuse that Solvay, founded in 1881, built this country's first soda ash plant.

In recent years a modernization and expansion program has taken place at Solvay's Syracuse works, and new plants have been built in other areas.

An entirely new soda ash plant, one of the world's largest, was completed this year at Syracuse, and modern facilities have recently been constructed there for production of chlorine, potassium carbonate, sodium sesquicarbonate, ammonium bicarbonate, and calcium chloride.

Metalweld Qualified Applicators for Amercoat

The MW Protective Coatings Div. of Metalweld, Inc., Scotts Lane and Abbottsford Ave., Philadelphia 29, Pa., who have been distributors as well as qualified applicators for Amercoat's complete line of vinyls, baked phenolics, and catalyzed epoxies since 1945, announces that they will continue as applicators of Amercoat coatings although the distribution of these products has been transferred to the O. F. Zurn Co., 2736 No. Broad St., Philadelphia 32, Pa.

Specialized Rolling Equipment

Marking the first step in the development of a specialized fabricating facility devoted exclusively to the rolling and forging of titanium, the Titanium Metals Corp. of America has placed an order for a Sendzimir reversing cluster mill for the cold rolling of continuous bands of titanium sheet in widths up to 49 in. This unique unit will be designed specifically to cold roll large coils of titanium to the extremely accurate gauge tolerances and mirror finish long

desired by the airframe industry. The mill will cost over $3,000,000.

The new rolling unit will be engineered by Allegheny Ludlum Steel Corp., one of the co-owners of TMCA, and will be installed in an Allegheny Ludlum Pittsburgh-area mill.

International Salt Research Lab.

A new laboratory for research and development concerning salt and related fields was opened on January 3, it was announced by Mr. Edward L. Fuller, President of the International Salt Co., largest salt producer in this hemisphere. At the new laboratory, located at 254 W. 31st St., New York City, International Salt scientists will attempt to solve many of the problems constantly arising from the production and uses of salt. It is estimated that there are already 10,000 uses for the company's basic product. The scientists will also work on many new ideas. The laboratory will be under the direction of Dr. Kurt Ladenburg, International's Director of Research.

DIVISION NEWS

Electronics Division

The Committee on Bylaws (A. P. Thompson, H. R. Harner, and J. R. Musgrave) recommends the following revisions. These revisions will be voted on at the Annual Meeting of the Division during the San Francisco convention and will take effect at the spring 1957 convention.

Article III, Section 2

Replace with:

"The terms of office shall be two years. The Secretary-Treasurer may serve successive terms. Other officers shall be eligible for re-election but shall not serve two successive terms."

(Note: Previously the term of office was one year; the change is recommended to be in line with the other Divisions and to insure continuity of effort. The re-election provision for the Secretary-Treasurer is made to retain the original intent.)

J. R. MUSGRAVE

The Nominating Committee (A. L. Smith, Chairman, H. R. Schoenfeldt, and J. F. Hazel) has selected the following nominees for officers during the 1956–1957 term:

Chairman—Arthur E. Middleton, P. R. Mallory & Co., Inc., Indianapolis 6, Ind.

Vice-Chairman (Luminescence)—Luke Thorington, Westinghouse Electric Corp., Bloomfield, N. J.

Vice-Chairman (General Electronics)—Lyle W. Evans, Sylvania Electric Products Inc., Seneca Falls, N. Y.

Vice-Chairman (Semiconductors)—Michael F. Lamorte, Westinghouse Electric Corp., Pittsburgh, Pa.

The term of office of Secretary Treasurer has two more years to run. This office is now filled by M. F. Quaely, Westinghouse Electric Corp., Bloomfield, N. J.

Each nominee has given assurance of his willingness to serve if elected.

The Bylaws of the Division provide that additional nominations may be made by petition signed by five members of the Division. Such petitions must be in the hands of the Nominating Committee before the election, and the nominees must have given assurance of their willingness to serve if elected.

The election will be held at the business meeting of the Electronics Division during the Spring Meeting of the Society in San Francisco, April 29–May 3, 1956.

M. F. QUAELY,
Secretary-Treasurer

1956 Extended Abstracts

The Electronics Division will again publish an "Enlarged Abstracts" booklet for the Spring 1956 convention of the Society at San Francisco. The booklet will have 1000-word abstracts of the papers to be presented before the Electronics Division in its symposia on

Luminescence

Semiconductors

The abstracts will contain pertinent information and experimental data given in the papers, and will provide these details before publication, thus aiding workers in the field. The abstracts will be "printed but not published."

The abstract booklets should be available by about April 12; the price will be $2.00. Orders should be sent to:

Martin F. Quaely
Research Dept., Lamp Div.
Westinghouse Electric Corp.
Bloomfield, N. J.

* * *

The Theoretical Electrochemistry Division is publishing an extended abstracts booklet of the papers to be presented at the sessions of the Theoretical Division at the Spring 1956 meeting of the Society in San Francisco. The booklet will also contain abstracts of the papers to be presented at the Symposium on "Adsorption Phenomena at Electrode Surfaces" sponsored jointly by the Theoretical Electrochemistry and Corrosion Divisions.

The extended abstract booklets can be obtained after April 16 at $2.00 each from:

Ernest Yeager
Dept. of Chemistry
Western Reserve University
Cleveland 6, Ohio

and will be available at the registration desk at the San Francisco Meeting.

Electrothermics and Metallurgy Division San Francisco Meeting Symposia

The Electric Arc in Inert Atmospheres and Vacuum

The Electrothermics and Metallurgy Division of the Society has planned a comprehensive symposium on electric arcs at its Spring Meeting to be held at the Hotel Mark Hopkins in San Francisco, April 29 to May 3, 1956. This Division, in cooperation with the Society, has made a special effort to make the meeting in San Francisco attractive to people from the East and West. As an added attraction to the technical program, the Society has made arrangements for several activities of a lighter nature for the enjoyment of members, guests, and ladies.

In general the technical program has been designed to treat the area of arc technology concerned with the theory, characteristics, and applications of high current arcs, the anode, cathode, and plasma of which are contained in a gas envelope under pressure or vacuum. Although the subject matter was originally limited to arcs in inert atmospheres and vacuum, it was considered desirable to widen its scope to include gases which produce reactions in one or more regions of the arc.

The following preview of the papers outlines the subjects covered by the two-day symposium on arcs:

1. A film presentation of the mecha-

Officers of Divisions of the Society

Battery

N. C. Cahoon, Chairman
U. B. Thomas, Vice-Chairman
E. J. Ritchie, Sec.-Treas.
The Eagle-Picher Co.
Joplin, Mo.

Corrosion

T. P. May, Chairman
J. E. Draley, Vice-Chairman
C. V. King, Sec.-Treas.
Dept. of Chemistry
New York University
New York 3, N. Y.

Electric Insulation

L. L. Deer, Chairman
D. A. Lupfer, Vice-Chairman
L. J. Frisco, Sec.-Treas.
The Johns Hopkins University
1315 St. Paul St.
Baltimore 18, Md.

Electrodeposition

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National Bureau of Standards
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Channing Dichter, Vice-Chairman
(General Electronics)
F. J. Biondi, Vice-Chairman
(Semiconductors)
M. F. Quaely, Sec.-Treas.
90 Mt. Hebron Rd.
Montclair, N. J.

Electro-Organic

H. M. Scholberg, Chairman
Stanley Wawzonek, Vice-Chairman
G. W. Thiessen, Sec.-Treas.
Dept. of Chemistry
Monmouth College
Monmouth, Ill.

Electrothermics and Metallurgy

A. C. Haskell, Jr., Chairman
A. U. Seybolt, Vice-Chairman
G. M. Butler, Vice-Chairman
E. M. Sherwood, Sec.-Treas.
Battelle Memorial Institute
Columbus 1, Ohio

Industrial Electrolytic

Milton Janes, Chairman
W. D. Sherrow, Sec.-Treas.
Great Lakes Carbon Corp.
Niagara Falls, N. Y.

Theoretical Electrochemistry

E. B. Yeager, Chairman
Paul Delahay, Vice-Chairman
Ralph Roberts, Sec.-Treas.
Office of Naval Research
Washington, D. C.

nisms of metal transfer in consumable-electrode arcs.

2. A paper describing the mechanism in high intensity arcs whereby electrical input energy is transferred to the electrode material.

3. A study of the rates of burn-off of anode and cathode at various subatmospheric pressures with particular application to titanium and zirconium arc melting furnaces.

4. The results of an investigation of the effect of magnetic fields on the behavior of the arc and molten pool in the consumable-electrode arc melting process.

5. A paper describing studies of the thermal environment of material vaporized by the high intensity arc with special emphasis on conditions prevailing in the anode tail flame.

6. The study of arc characteristics as affected by different electrode materials in argon and reduced pressure including a high-speed film presentation.

7. A study of the characteristics and thermal dissipation properties of high current arcs in the five rare gases.

8. A paper on the high intensity arc in process chemistry which presents interesting applications in chemical and metallurgical processes.

9. A study of the effect of variables on the melting rate of metals, such as kind of metal, crucible to electrode size ratio, power input, etc., in the consumable-electrode arc furnace.

10. A discussion of the pressure relationship in the regions above and within the vacuum arc as applied to arc melting furnaces.

11. A paper and film presentation describing the vacuum remelting of superalloys and steels by the consumable-electrode process in terms of a comparison of the properties, gas contents, and cleanliness of air-melted and vacuum remelted materials.

12. An experimental study of a three-phase a-c consumable-electrode arc furnace and its economic and practical advantages.

13. A paper describing the construction and operation of a unique general purpose laboratory and pilot-plant arc furnace for melting in protective atmospheres and vacuum.

14. A paper treating economic and reaction considerations of electrode requirements of the high intensity arc for metallurgical applications.

15. A paper discussing electrode control systems for inert atmosphere and vacuum arc furnaces in terms of operating characteristics and relative merits of the various regulator types.

We believe the above subject matter should arouse considerable interest because of the expanding applications of arc technology in the processing of modern metals.

WILLIAM E. KUHN,
Program Chairman

Marginal Ores and Their Relation to the National Economy

The rapid depletion of high grade ore deposits has resulted in a renewed emphasis on the low grade deposits often classed as "marginal." Improved technology for recovering valuable ore constituents and the new emphasis on minor metals make this symposium of increasing importance.

Stephen M. Shelton, Regional Director, Region I, U. S. Bureau of Mines, Albany, Oreg., will be the keynoter for the meeting. In addition to Bureau activities, Mr. Shelton is well known for his role in the production of zirconium and the development of ore reserves and metallurgical processes in the Northwest.

The eight papers to be discussed at the Society Meeting in San Francisco include subjects ranging from power resources for the development of electrolytic plants in Alaska to the separation of thorium and rare earths from ores and their ultimate reduction to metal.

The symposium chairman will be A. H. Roberson, Chief, Branch of Process Metallurgy, U. S. Bureau of Mines, Albany, Oreg.

A. H. ROBERSON

Atomic Reactor Fuel Processing Metallurgy

A half-day session on the pyrometallurgical processing of atomic reactor fuels will be part of the technical program for Wednesday morning, May 2, during the annual Spring Meeting in San Francisco.

The Society has been fortunate in obtaining the results of outstanding work by prominent AEC-sponsored scientists on the critical subject of reprocessing reactor fuels. This is the first session on this subject to be presented before a regular technical society.

The subject matter is of critical interest to anyone who may be concerned with the chemistry or metallurgy of reactor fuel components, and particularly with the separation of the unused uranium or plutonium fuel material from fission products and other parts of the fuel structure.

Several techniques will be presented, including distillation, magnesium extraction, salt extraction, electrorefining, and liquid metal extraction.

A. U. SEYBOLT

Rare Earth Symposium

A symposium on the production, physical properties, and chemistry of the rare earths will be held as part of The Electrochemical Society program at San Francisco. The program will include treatment of ores, production of metal, flame spectrometry, and the formation of lanthanum compounds.

Recent expanding interest in rare earths should promote stimulating discussions.

A. U. SEYBOLT

SECTION NEWS

Detroit Section

A talk on the subject "Vapor Plating" was presented before the Detroit group on November 18, 1955, at Wayne University. The speaker of the evening was Dr. Ivor Eugene Campbell, Chief of the Division of Inorganic Chemistry and Chemical Engineering at Battelle Memorial Institute. At the offset, a distinction was made between vapor plating and vacuum metallizing in that, with the former, the work is maintained at a higher temperature than the plating material. A typical reaction in the vapor plating process is:

$$TaCl_5 + H_2 \xrightarrow{\Delta} Ta + HCl$$

The temperature at which the evaporation is carried out for the above reaction is about 200°C, whereas the reduced metal deposits on a surface maintained between 900° and 1000°C. Vapor plating is therefore a chemical process involving reduction by hydrogen or thermal decomposition; vacuum metallizing involves a physical process. A prerequisite for vapor deposition is that the compound of the material to be plated is volatile. The process has been used to obtain such metals as Ti, Hf, Mo, Cr, Ce, Pt, Ir, Cb, Ta, V, Th, W, and Zr, and such compounds as carbides, nitrides, borides, silicides, and oxides. Less refractory metals such as Al, Sn, Pb, Fe, Cu, and As have been obtained. Only thin coatings of metal can be formed; otherwise spalling will occur.

At the present stage of development, vapor plating cannot compete with electrodeposition, except in very specific cases where the latter is inadequate. Both nickel and iron are practically plated by carbonyl decomposition. Chromized steel is the main commercial application to date. An excellent application of vapor plating lies in the preparation of high purity metals.

M. SHAW, *Secretary-Treasurer*

New York Metropolitan Section

A regular meeting of the Metropolitan Section was held on November 16, 1955. Guest speaker was Dr. Harry P. Gregor of the Polytechnic Institute of Brooklyn. His subject was Ion Exchange Membranes.

Modern views on the behavior of "permselective membranes" are generally based upon the fixed charge theory and not upon the adsorption of ions from solutions. A review of the classical work of Michaelis can be interpreted in that sense. The partially oxidized collodion membrane and similar substances behave as permselective barriers due to potentially dissociable fixed groups. This is confirmed by work in later years by K. Sollner on membranes of a similar type.

The speaker explained in very instructive, simple terms how the newer membranes, with a much higher fixed charge group activity, behave according to Gibbs Donnan equilibria and how the electrochemical potential on the membrane is defined by Nernst's equation.

Extensive studies at Brooklyn Polytechnic, conducted by the speaker, led to new types of membranes and to special membranes of selective activity. Nevertheless, natural membranes, such as cell walls, exhibit still much higher selectivity and efficiency.

Referring to practical applications, the speaker pointed out that theoretically many uses of these membranes can be visualized. However, the present high cost interferes with a large-scale industrial application. But the development of cheaper and highly active permselective membranes would undoubtedly lead to commercial uses.

In special instances where fresh water is not available, the production of potable water from brackish water has been successfully introduced.

R. O. BACH

Niagara Falls Section

Fall Roundup was held at the Youngstown Yacht Club on September 14, 1955. Thirty-eight members attended the meeting which featured tap beer and a buffet supper.

Mr. R. J. Cooksley, Public Relations Officer of the Hydro-Electric Power Commission of Ontario, gave an excel-

lent talk on the new power development along the St. Lawrence River.

The history of the development of the present undertaking was traced, and note was made of the fact that Canadian Hydro engineers drew a plan very similar to the present one in the year 1913. Interesting incidents in the displacement of 6500 people on the Canadian side were recounted. Land upon which three towns at present stand will be flooded. The fact that control dams will stabilize the water level of Lake Ontario should interest lakeshore residents.

Many Kodacolor prints of operations and the St. Lawrence area were shown.

A dinner meeting of the Niagara Falls Section was held at the Red Coach Inn on October 19, 1955. The attendance at dinner was 63.

The program for the evening consisted of a short series of talks by representatives of the five major graphite and carbon producers in the area. Members enjoyed a stimulating evening as evidenced by the thought-provoking questions. Topics covered were as follows:

1. Graphite Specialties—Myron Cory. Manufacture and special properties of "Graph-i-tite," a carbon-impregnated graphite for high temperature use.

2. Great Lakes Carbon—L. Juel. Results of experimentation in improved mercury cell graphite anode joints.

3. International Graphite and Electrode—R. McGhee. Problems involved in manufacture of furnace electrodes.

4. Natural Carbon (three technicolor pictures). Curry Ford—improved Karbate design; Neal Johnson—new National Carbon laboratory at Niagara Falls; Bill Palmquist—Q-anodes for cathodic protection of pipelines.

5. Stackpole Carbon—Dr. Krellner. There was discussion of the properties of graphite for mechanical seals. Many unusual shapes were displayed. A booklet enumerating properties of graphite was made available.

A dinner meeting of the Niagara Falls Section was held at the Red Coach Inn on November 16, 1955. There were 33 present.

Mr. R. B. MacMullin announced a plant trip through the Carbide Division of the Electro Metallurgical Co. on December 14.

The speaker, James Moore, was introduced by Arthur Haskell. Mr. Moore, General Manager of Vacuum Metals, Inc., gave a fine talk on "Vacuum Metallurgy." In his introduction he grouped vacuum metallurgy into four major fields: (*a*) vacuum thermal reduction, e.g., calcium, magnesium; (*b*) vacuum evaporation, e.g., thin films; (*c*) vacuum heat treating, e.g., annealing; (*d*) vacuum melting and casting.

Also mentioned as the start of a fertile field was ladle degassing to remove hydrogen from steel for use in large castings and forgings.

The status of the present consumable-electrode vacuum arc furnace as developed by Allegheny Ludlum was noted as a pioneering effort in another potentially large field.

The major portion of the talk was concerned with vacuum melting and casting techniques. Carbon deoxidation of superalloys was explained. Equilibrium relationships between gas content of simple solutions and vapor pressure were shown. The complex role of refractory disassociation was noted.

Instances in which specific vacuum-melted superalloys proved much better than the same composition air-melted alloys were tabulated. To date, vacuum-melted alloys were shown to have a distinct advantage for fatigue and dynamic loading applications as well as for bearings used in jets.

Lastly, it was pointed out that in some cases vacuum-melted superalloys containing less strategic metals could be substituted for air-melted superalloys.

An informal get-together of the Niagara Falls Section was held at the Electro Metallurgical Co. on December 14, 1955. An extremely stormy and slippery night limited attendance to 25 persons.

High light of the evening was a plant tour of the calcium carbide manufacturing facilities of the Electro Metallurgical Co. The flow of raw materials was followed from the coke drying system with its million-dollar dust collection system through the mix weighing and distribution system to the modern covered furnaces. Operation of the furnace and tapping of the calcium carbide were observed.

Refreshments were served after the plant tour.

L. A. Stoyell,
Secretary-Treasurer

Philadelphia Section

At the meeting on January 4, 1956, the Philadelphia Section of the Society participated in the world-wide observance of the 250th anniversary of the birth of Benjamin Franklin which occurred on January 15, 1956.

After a social hour and dinner at the Lenape Club, members and guests were privileged to make a tour of inspection of the excellent new physics building of the University of Pennsylvania. This feature was arranged and conducted by Professor William Stephens, head of the Physics Department, with the aid of a group of graduate students.

When the audience, numbering about 75, had assembled in the auditorium, Chairman E. L. Eckfeldt thanked Professor Stephens and called on him for some remarks. Professor Stephens spoke of the appropriateness of honoring Benjamin Franklin at this time. Franklin, founder of the University of Pennsylvania and originator of its department of "natural philosophy," displayed many facets, not the least of which was his constant interest in science. Though he might have been amazed at modern technological advances, there can be no question of his ability to have grasped their significance or of the fascination with which these developments would have gripped him. Professor Stephens thus pointed to the aptness of the subject, "The Industrial Future of Atomic Energy," and introduced the speaker, Dr. David S. Ballantine.

Dr. Ballantine, of the Nuclear Engineering Dept. at Brookhaven National Laboratory, prefaced his talk with the observation that the ramifications of atomic energy developments were such as to demand the breadth of interest and character displayed by Franklin, if one man were to be put in charge of them on an international scale. The tone of Dr. Ballantine's presentation is best shown in a few of the opening paragraphs of his talk.

"A decade ago the atomic age was considered by the average citizen in terms of the megatons of explosive power which could be concentrated in a sphere of nuclear material smaller than a soccer ball. This was a natural outgrowth of the stories and photographs of the vast devastation wrought at Hiroshima and at Nagasaki, and the subsequent A-bomb tests on the Pacific atolls.

"However, even in the earliest days of the atomic age the tremendous peacetime potential was realized by the scientists and engineers who had helped to fashion U^{235} and Pu^{239} into weapons of war. It was realized that the neutrons which are produced in the fission of the uranium and plutonium

nuclei could, under controlled conditions, become a powerful scientific research tool. The mass of radioactive fission products, so dangerous because of their lethal beta and gamma radiations, could, in small quantities and in a shielded environment, become valuable tracers or sources of ionization energy. And the heat produced in such prodigious quantities from small amounts of material foreshadowed a complete revolution in the power picture of the future.

"It is upon these three building blocks, neutrons, radioactive fission products, and nuclear heat that the future of atomic energy has been built. As this field develops it will reach out and intimately affect the philosophy and actions of the chemical manufacturer, the metallurgist, the shipbuilder, the aircraft industry, the food and drug industries, the lawyer, the insurance man, the physician, the politician, and the average citizen. It is the objective of this paper to discuss the extent to which this force of atomic energy has already been felt and the ways in which it will be felt in the near and far distant future."

Dr. Ballantine then expounded on the applications of the three types of energy and his dissertation was received with great interest by the audience.

G. W. Bodamer, *Secretary*

Washington-Baltimore Section

The 36th technical meeting of the Section was held on December 15, 1955 at the National Bureau of Standards. The first speaker of the evening was Dr. W. R. Graner of the Bureau of Ships who spoke on the mechanical properties of laminates. Dr. Graner briefly described the chemistry of plastics and the poor mechanical properties of unreinforced materials. Several types of reinforcements are used in fabricating laminates, and extensive data were presented describing the mechanical properties of the laminates that exceed those of aluminum and steel in some instances. Fabricated laminates in use today include sonar domes, boats, storage tanks, floats, and piping.

The second speaker was Dr. J. P. Hoare of the Naval Research Laboratory whose topic was the hydrogen-palladium electrode. Palladium metal undergoes a phase change in the presence of hydrogen gas, and the initial potential exhibited by pure palladium electrodes in sulfuric and hydrochloric acids is determined by the hydrogen concentration in the metal. Electrochemical evidence indicates that the change from the "high hydrogen" phase to the "low hydrogen" phase occurs spontaneously upon exposure to the acid solutions regardless of the pressure of hydrogen maintained above the solution. Anomalous electrochemical observations with palladium electrodes are explained on the basis of these observations.

The third speaker of the evening was Dr. J. M. Sherfey of the National Bureau of Standards who described the application of calorimetry to the study of electrochemical reactions. In this new technique the temperature change occurring during an electrochemical reaction is measured simultaneously with the voltage and current usually recorded in the study of cell reactions. Thus the electrochemical process may be considered from a thermodynamic view, and the ΔH of the reaction and cell polarization may be calculated. The copper cyanide complexes have been studied by this technique.

Jeanne Burbank, *Secretary*

NEW MEMBERS

In January 1956 the following were approved for membership in The Electrochemical Society by the Admissions Committee:

Active Members

William M. Albrecht, Battelle Memorial Institute, 505 King Ave., Columbus 1, Ohio (Corrosion, Electrothermics & Metallurgy)

Thomas T. Anderson, Aluminum Co. of Canada, Ltd., Arvida, P. Q., Canada (Industrial Electrolytic)

Robert F. Ayres, Oakite Products, Inc.; Mail add: 264 Broad Ave., Leonia, N. J. (Corrosion)

Jose P. R. Cels, Kemet Co., Div. of Union Carbide & Carbon; Mail add: 3139 E. Overlook Rd., Cleveland 18, Ohio (Electronics)

Bruce J. Garvey, General Dry Batteries, Inc.; Mail add: 18802 Berncliffe Ave., Cleveland 11, Ohio (Battery)

Edward Heinzelman, Jr., Oakite Products, Inc.; Mail add: 276—8th St., Palisades Park, N. J. (Corrosion)

Clarence H. Helbing, Pittsburgh Plate Glass Co.; Mail add: 68 Hemlock Lane, Bay Shore, N. Y. (Battery)

Thomas A. Henrie, Union Carbide Metals Research Lab., Box 580, Niagara Falls, N. Y. (Theoretical Electrochemistry)

Polykarp Herasymenko, Research Div., Research Bldg. No. 1, New York University, 178 St. & Cedar Ave., New York 53, N. Y. (Electrodeposition, Electrothermics & Metallurgy, Theoretical Electrochemistry)

Stanley Hills, Reduction Research Lab., Reynolds Metals Co., Sheffield, Ala. (Theoretical Electrochemistry)

Cecil Jenkins, General Dry Batteries Inc.; Mail add: 1452 Wayne Ave., Lakewood 7, Ohio (Battery)

Stanley Kass, Westinghouse Atomic Power Div.; Mail add: 1115 Morningside Ave., Pittsburgh 6, Pa. (Corrosion)

Richard L. Mansfield, National Carbon Co., Clarksburg, W. Va. (Electrothermics & Metallurgy)

Philip A. Nelson, Boeing Airplane Co.; Mail add: 1516 W. 67th St., Seattle 7, Wash. (Electrodeposition)

Thomas D. Parks, Clorox Chemical Co., 850-42nd Ave., Oakland 1, Calif. (Corrosion)

Louis Peselnick, Power Condenser & Electronics Corp., 514-10th St., N. W., Washington 4, D. C. (Electric Insulation)

Herbert M. Pollack, Radio Corp. of America; Mail add: 672 Watkins St., Brooklyn 12, N. Y. (Electronics, Theoretical Electrochemistry)

Alva H. Roberson, U. S. Bureau of Mines; Mail add: 3242 Crest Drive, Corvallis, Oreg. (Electrothermics & Metallurgy)

Edgar J. Seyb, Jr., Metal & Thermit Corp.; Mail add: 23061 Norwood, Oak Park 37, Mich. (Electrodeposition)

David H. Thompson, Corrosion Research Lab., The American Brass Co., Waterbury 20, Conn. (Corrosion)

Geoffrey R. Ward, Research Lab., Gillette Safety Razor Co., Boston, Mass. (Corrosion)

William P. Wene, Sangamo Electric Co., Marion, Ill. (Electric Insulation)

Lewis C. Wood, Kennecott Copper Corp.; Mail add: 1219 E. 4th South, Salt Lake City 2, Utah (Electrodeposition, Electronics, Electrothermics &

A recent action of the Board of Directors of the Society requires that, commencing January 1, 1956, all prospective members include first year's dues with their applications for membership.

Also, please note that, if sponsors sign the application form itself, processing can be expedited considerably.

Metallurgy, Industrial Electrolytic, Theoretical Electrochemistry)

SHIRO YOSHIZAWA, Duke University; Mail add: 2511 Chapel Hill Rd., Durham, N. C. (Battery, Corrosion, Electrodeposition, Industrial Electrolytic, Theoretical Electrochemistry)

Associate Member

CARL F. CLINE, Carborundum Co.; Mail add: 2729 Forest Ave., Niagara Falls, N. Y. (Electrothermics & Metallurgy)

Student Associate Member (Awarded by the Cincinnati Committee)

ROBERT J. MORRIS, University of Cincinnati; Mail add: 517 Riddle Rd., Cincinnati 20, Ohio (Electrodeposition)

Reinstatement to Active Membership

ELWOOD R. RINEHART, Chance Vought Aircraft; Mail add: 1515 Tulip, Arlington, Texas (Corrosion, Electrodeposition)

Deceased Members Reported in December 1955

A. E. CHESTER, Waukegan, Ill.
EDWARD R. COLE, Lake Worth, Fla. (Emeritus Member)
REGINALD O. ELLIS, Sydney, Australia

PERSONALS

LAWRENCE M. LIGGETT, formerly Research Supervisor at Wyandotte Chemicals Corp., has joined the Speer Carbon Co., St. Marys, Pa., as Manager of Research.

BERTRAM C. RAYNES has been named Head of the Dept. of Chemical Engineering of Horizons Inc., Cleveland, Ohio. He had been serving as a section head in the Dept. of Metallurgy. The Dept. of Chemical Engineering, in charge of process development, among other projects, at present is working on the beneficiation of ilmenite (titanium) ores.

AARON WACHTER, Shell Development Co., Emeryville, Calif., has been given the 1955 Outstanding Service Award of the Western Region of the National Association of Corrosion Engineers. Dr. Wachter, immediate past president of NACE and long active in the association in administrative and technical capacities, received the award at the Western Region's 5th Annual Corrosion Conference Banquet on November 17, 1955, in San Francisco, Calif.

IRWIN GOLDMAN has been appointed Manager of Technical Planning for the Research Labs. of Sylvania Electric Products Inc., New York City. Mr. Goldman's responsibilities in his new assignment include review of technical programs, liaison activities including coordination of sales and sales contacts, and the preparation of engineering programs and budgets for the laboratories. Prior to his new appointment, Mr. Goldman was head of technical services of Sylvania's Physics Lab.

C. BRUCE BROWN has accepted a position with R. Campbell & Associates Reg'd., Montreal, Canada. Prior to this he was Vice-President and Assistant General Manager at the Standard Chemical Co. Ltd. in Montreal.

RAYMOND C. HAEFNER has joined The Electric Autolite Co., Toledo, Ohio, as Sales Engineer—Detroit Area. Previously he was Plant Engineer at the Autolite Battery Corp. in Niagara Falls, N. Y.

LETTER TO THE EDITOR

A Cell for Measuring the *p*H of Solutions Corrosive to Glass

Dear Sir:

Recent work in our laboratory required *p*H measurements on solutions which are corrosive to glass. Our problem was that most conventional salt bridges and reference electrodes which are immersed in solutions to make up *p*H cells are fabricated from glass. The corrosive reactions at the glass-liquid interface of such bridges or electrodes immersed in the solutions of interest to us would increase the *p*H of these solutions and decrease the lifetime of the *p*H cell. For this reason we have devised an emf cell with no glass-liquid interfaces in the corrosive medium.

Essentially our cell is

Pt/Q, QH_2, unknown solution	saturated KCl, Hg_2Cl_2/Hg,

where the dotted line refers to a new type of liquid junction between the unknown solution saturated in quinhydrone and the saturated potassium chloride solution. The unknown solution is contained in a Lucite vessel shaped like a Buechner funnel. Tygon tubing is connected to the stem of the Lucite vessel so that the unknown solution is held in place by squeezing this tubing with a screw clamp. The other side of the tygon tubing is connected to a glass vessel, also shaped like a Buechner funnel, which is filled with potassium chloride solution and which contains a commercial saturated calomel electrode. Junction between the unknown and the potassium chloride is effected by adjusting the screw clamp. To accomplish this, however, it is necessary to insert a platinum wire in the center of the tygon tubing, so that, by applying the screw clamp at a section of the tubing which contains the platinum wire, a fraction of its length is in the quinhydrone side of the tubing and a fraction in the potassium chloride side. This procedure affords good liquid junction by a slow trickle of one solution into the other. To eliminate the effects of these unknowns on the calomel electrode it was found advantageous to direct the potassium chloride into the corrosive medium instead of vice versa, by a slight hydrostatic pressure head.

The emf readings of this cell may be taken with any potentiometer. The quinhydrone chamber is emptied regularly between runs or for overnight storage, and cleaned. The potassium chloride may be emptied, replenished, or replaced as frequently as required. The best emf readings are obtained from 5 to 15 min after making up a cell. Duplicate measurements obtained by emptying and refilling the quinhydrone chamber usually checked to within ± 0.05 *p*H units. A known, noncorrosive, *p*H 4 buffer was checked to within 0.03 *p*H units of its certified value.

ALAN L. ROTHMAN
LEROY I. BRADDOCK*
Glass Div., Research Lab.
Pittsburgh Plate Glass Co.
Creighton, Pa.

*Present address: Mine Safety and Appliance Co., Pittsburgh, Pa.

BOOK REVIEWS

THE METALLURGY OF MAGNESIUM by Ch. L. Strelez, A. J. Taiz, and B. S. Guljanizki, translated from the Russian. Published by VEB Verlag

"EVEREADY" BRAND BATTERY DEVELOPMENT

CHEMICAL AND MECHANICAL ENGINEERS

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PRODUCT DESIGN AND MACHINE DESIGN

Product and Process Development Department in Cleveland has openings for Chemical and Mechanical Engineers with two to five years experience. Work is concerned with both new product design and the development of production equipment for primary power supplies to be used with transistorized electronic equipment, portable light sources, capacitors and a wide range of electronic apparatus.

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Bachelor or graduate degrees considered. Send resumé of educational background and work experience to:

•

National Carbon Co.
Division of Union Carbide and Carbon Corp.
P. O. Box 6056, Cleveland 1, Ohio

Technik, Berlin, 1953. 451 pages. Price: 33 West Marks.

This well-documented Russian monograph is an attempt at gathering all available data on magnesium production methods. It is written for the metallurgist, scientist, and for students. For the latter, emphasis is put on thermodynamic calculations and heat balances.

The introduction contains the usual Soviet propaganda. It claims that the capitalist world kept all magnesium production methods strictly secret, so that the U. S. S. R. had to start from scratch. Of course. The U. S. A., France, Japan, and Norway had to do the same, while apparently England could buy German experience. That is the essence of the competitive system. The communist "generosity" of now publishing "their" data is suspicious at first sight, and on more careful examination of this book one discovers the predatory methods of the system. The authors are experts in plagiarizing and pillaging world publications. They mix their own poor brew with the stolen information so intimately that even the expert has trouble finding out what is the Soviet research. Pictures are taken from American and German publications with no acknowledgment and woven in the description of Russian plants to make believe that this is the way things are done in Soviet Russia. Only three non-Russian names could be found in the text and the bibliography contains 62 references, all Russian except three. The Russian, Beketoff, is claimed to be the father of magnesium, because he produced the metal by potassium reduction of the oxide, quite an impossible performance. Bussy, who produced the first compact metal by reduction of the chloride, is ignored, as is Bunsen, who with his genial arrangement of claypipe, iron cathode wire, and carbon rod anode laid down the principle of our actual magnesium cells. The method of the I.G. Farbenindustrie, who are the founders of magnesium industry, is expropriated by the authors, and the name of the company is never mentioned. The Soviets stole the plants of this company, kidnapped their personnel in part, and one Dr. Schichtel is mentioned as the scientific editor of the rather poor translation of this book. The work done in the U. S. A. as to magnesium production methods is put off with the remark that it contributed nothing. The textbook of Gmelin on the chemistry, from which much is taken, and the one by Beck on the alloys, are not mentioned, while Powell is reported once. Guntz, who gave the basic idea of the silico thermic reduction method, Matignon, who ran the first retort by this process, are skipped, but Pidgeon is mentioned. Hansgirg, the pioneer of carbothermic reduction, is ignored. Incense is burned in many places to the bosses of the soviet research hierarchy, making believe that this crowd gave magnesium to the world.

This book can, however, be recommended as a good compilation of data since a similar monograph does not exist this side of the iron curtain. It is divided in the following sections: I. Raw materials, 49 pp.; II. Electrolytic processes, 125 pp.; III. Thermal magnesium by Si, Al, and CaC_2 reduction, 84 pp.; IV. Thermal magnesium by carbon reduction, 69 pp.; V. Properties, alloys, melting, refining, 25 pp.

The second section contains chapters on the production of carnallite, hydrated chlorides, dehydration in general, pure magnesia, charge preparation for the chlorination, the chlorinator and its operation, properties of the electrolyte such as specific gravity at temperature and relatively to magnesium, electric conductivity, decomposition voltage, solubility of magnesium in the bath, obnoxious impurities, influence of temperature on the electrolysis, cell construction, anode and cathode arrangements, plant outlay and operation, transportation of materials to and from the cells, thermal balances.

The third section concerns properties of the batch used for Si, Al, or CaC_2 reduction, briquetting, thermal conductivity, fusibility, electric conductivity, basic theory, thermodynamics, velocity of the reaction, temperature pressure function, preparation of the charge, and furnace types.

The fourth section refers to quality requirements of the batch used in carbothermic reduction, its physical chemistry, process technology, compacting the condensate, and subliming magnesium. Section five treats the fusion, fluxes, refining by subliming.

Some of the chapters can be recommended for special attention. The physics of dehydrating magnesium chloride and carnallite are well described as are the construction and operation of the cell. A vertical retort arrangement for producing silicothermic magnesium deserves consideration. An 8000-kw carbothermic arc furnace for magnesium production is discussed. It probably never worked successfully. Typically, no calculation of the cost is given nor anything about the number of workmen needed. Paper, print, and illustration are up to the standards. This book belongs in the book shelf of anybody interested in the practical aspects of magnesium production, and it may attract all those who today consider recycling $MgCl_2$, obtained in the magnesium reduction of $TiCl_4$.

The reviewer wants to add an admonition for those responsible in our country for keeping our students and our technical staffs in universities and industry informed. It would be bad indeed if these had to draw their knowledge on magnesium production from a Russian book because editing such a book here does not pay. We lack up-to-date monographs on the descrip-

tive metallurgy of aluminum, sodium, lead, zinc, and ferroalloys. Could it be that emphasis in our universities put today on thermodynamics, physical chemistry in general, and on "unit operations" in chemical engineering has driven from the market descriptive books on the winning of the above-mentioned metals? This would be bad for our generation of technicians who would know the laws, but not the processes to which they apply, nor the equipment in which they should be used. Could this be the reason why extractive metallurgists with know-how have become such a rare species?

W. J. KROLL

COMPREHENSIVE INORGANIC CHEMISTRY. Edited by M. Cannon Sneed and Robert C. Brasted. VOL. IV: ZINC, CADMIUM AND MERCURY by Howard M. Cyr; SCANDIUM, ITTRIUM AND THE LANTHANIDE SERIES by Thomas D. O'Brien. Published by D. Van Nostrand Co., Inc., Princeton, N. J., 1955. xii + 193 pages, $5.00.

Like the others in this projected eleven-volume series, this book attempts to cover the subject elements and their compounds thoroughly but briefly. Recent discoveries, methods, applications are mentioned; where any theory is given it meets current standards (as corrosion theory in connection with zinc, largely based on the "Corrosion Handbook"). Many pertinent references are given, though with no attempt to make the list complete. This book (and the series) will be useful to undergraduates and more experienced chemists alike, if they wish a survey more comprehensive than can be found in a single textbook, and if they do not expect too much.

METALURGIA GENERAL. EXTRACTIVA, FISICA, MECANICA Y QUIMICA by Emilio Jimeno and F. R. Morral. Published by University of Madrid, Madrid, Spain, 1955. xxiv + 1324 pages, 375 pesetas.

A comprehensive treatment on metallurgy, in two paper-covered volumes.

GLASS REINFORCED PLASTICS. Edited by Phillip Morgan. Published by Iliffe and Sons, Ltd., London, England, and Philosophical Library, Inc., New York, N. Y., 1954. 248 pages, $10.00.

Well described by the title.

THE ROGER ADAMS SYMPOSIUM. Published by John Wiley and Sons, Inc., New York, N. Y., 1955. ix + 140 pages, $3.75.

Papers presented at a Symposium in honor of Roger Adams at the University of Illinois by six of his former students who are now well-known chemists.

APROVECHAMIENTO DE LA ENERGIA ATOMICA by G. E. Villar. Published by Pan-American Union, Washington, D. C., 1955. 61 pages.

A survey.

HAWLEY'S TECHNICAL SPELLER by G. G. Hawley and A. W. Hawley. Published by Reinhold Publishing Corp., New York, N. Y., 1955. 146 pages, $2.95.

Correct spelling of some 8000 technical words, with a few pointers.

C. V. KING

ANNOUNCEMENTS FROM PUBLISHERS

TABLES OF SINES AND COSINES FOR RADIAN ARGUMENTS. National Bureau of Standards Applied Mathemathics Series 43. Order from Government Printing Office, Washington 25, D. C. 278 pages, 6 tables, $3.00.*

This publication is an extended and corrected reissue of TABLES OF SINES AND COSINES FOR RADIAN ARGUMENTS which was prepared by the Mathematical Tables Project of the Federal Works Agency, Works Progress Administration for the City of New York, under the sponsorship of the NBS. The original volume, published in 1940, is known as Mathematical Table MT4.

*Foreign remittances must be in U. S. exchange and should include an additional one-third of the publication price to cover mailing costs.

HYDROGEN CONTAMINATION IN TITANIUM AND TITANIUM ALLOYS, Part 1, Hydrogen Embrittlement in Alpha-Beta Titanium Alloys. Report prepared by the Wright Air Development Center, 1955. Order PB 111620 from Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C. 185 pages, $4.75.

Report of WADC technical meeting October 29, 1954, including papers, discussions, and illustrations.

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WATER POLLUTION ABATEMENT MANUAL, W-4. Published by the Manufacturing Chemists' Association, 1625 Eye St., N.W., Washington 6, D. C., 1955. 12 pages, 25 cents.

The manual, part of a continuing series, discusses such subjects as permissible concentrations, sources of oils and tars in plants, removal of separable oil from water, and disposal of oils.

LITERATURE FROM INDUSTRY

AMERCOAT® PROTECTIVE COATINGS. Illustrated catalogue describes the Amercoat method of controlling rust and corrosion. The various corrosion-resistant coatings systems manufactured by the company are described, and suggestions in regard to the selection of the proper protective coating and the preparation of coating specifications are outlined. Amercoat Corp. P-383

DIAMOND ALKALI CO. RESEARCH REPORT. A 6-page research report on Diamond Alkali Co. has been prepared by L. F. Rothschild & Co., members of the New York Stock Exchange. Among the topics covered are: research, product mix, labor relations, plant modernization and location, management, and comparative value. L. F. Rothschild & Co. P-384

METALLIC STEARATES. Comprehensive 36-page bulletin outlines the properties and uses of metallic stearates. It lists the composition of 46 metallic stearates, shows graphically the industries in which they are used, and presents an analysis of recommended applications. Other helpful data include an explanation of Witco's analytical procedures, government specifications for metallic stearates, shipping information, and a guide to other Witco products. Copies available upon letterhead request. Witco Chemical Co. P-385

HARDNESS CONVERSION TABLES FOR STEELS. Celluloid card, 2¾ in. x 4¾ in., gives approximate relationship between Brinell, DPH (Vickers), Rockwell, and Shore Scleroscope hardness values and corresponding tensile strengths of steels. Data from SAE Handbook. International Nickel Co., Inc. P-386

GLASSED STEEL TANK TRAILER. Bulletin describing a glassed steel tank trailer is offered. Use of acid-alkali resistant glass on the 2200-gal tank trailer permits handling of all acids except hydrofluoric, and alkalies up to *p*H 12. The durable glass inside the tank not only prevents corrosion in transit but also assures that the material will be delivered in its original pure state. Pfaudler Co. P-387

HORSE HEAD® BULLETIN. This issue features a story on the continuous galvanizing line, a highly automatic system of producing zinc-coated steel sheets at a rate of from 12 to 15 tons per hour. The subject of another article is a new photosensitive paper, developed by R.C.A. engineers, utilizing an unusual property of zinc oxide in the coating process. New Jersey Zinc Co. P-388

GERMANIUM RECTIFIERS. New 2-color, 4-page bulletin describes and illustrates germanium rectifiers. The germanium rectifier is the latest addition to H-VW-M's line of power equipment for electroplating, anodizing, and related processing. The folder explains the advantages of the rectifier and all its special features, its efficiency, voltage regulation, controls, cooling, and electrical protection. Hanson-Van Winkle-Munning Co. P-389

ELECTROPLATING DATA CHART. A time-saving chart designed to be invaluable in costing and every other operation connected with precious metal electroplating is being distributed. The new Technic chart provides at a glance all related and comparative data on gold, rhodium, palladium, platinum, silver, and nickel. Technic, Inc. P-390

LEFAX TECHNICAL DATA CATALOGUE FOR 1956. Revised catalogue of Pocket Size Technical Data Books is available. These handy reference books cover every branch of engineering, are comprehensive and authoritative. Each book contains approximately 140 pages of data, including current advances. Lefax Data Books sell for $1.25 each. Free catalogue on request. Lefax Publishers. P-391

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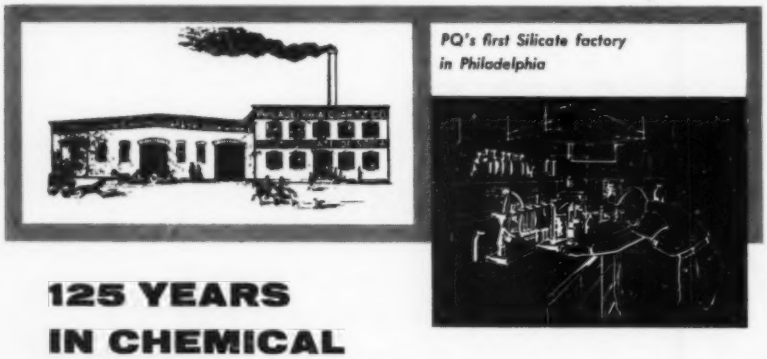

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TANTALUM CORROSION TEST KIT. A convenient kit for testing tantalum either in the laboratory or in process equipment is available. It consists of two pieces of 0.020 in. thick tantalum sheet, one 1 in. x 1 in., the other ½ in. x 4 in., and a length of 0.030 in. tantalum wire for attaching the specimens. The kit is available to production, pilot plant, or research technicians without charge. Fansteel Metallurgical Corp. N-251

SEMICONDUCTOR RESISTIVITY TEST SET. Model JN1 Resistivity Test Set is especially designed to measure the resistivity of germanium samples. The probe assembly can also be adapted for measurement of silicon. It covers a range of resistivity from 0.1 to 100 ohm-cm with a measurement accuracy of ±5%. Baird Associates, Inc. N-252

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(*Continued on page 86C*)

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CHEMIST OR METALLURGIST wanted to work at the National Bureau of Standards as a Research Associate of the American Electroplaters' Society. Post-graduate work or research experience required and background in physics or physical chemistry desired. Reply to Mr. Fielding Ogburn, National Bureau of Standards, Washington 25, D. C.

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Stackpole Carbon Company, St. Marys, Pa.

Standard Steel Spring Division of the Rockwell Spring and Axle Company, Coraopolis, Pa.

Stauffer Chemical Company, San Francisco, Calif.

Sylvania Electric Products Inc., Bayside, N. Y. (2 memberships)

Sarkes Tarzian, Inc., Bloomington, Ind.

Tennessee Products & Chemical Corporation, Nashville, Tenn.

Udylite Corporation, Detroit, Mich. (2 memberships)

United Chromium, Inc., New York, N. Y.

Vanadium Corporation of America, New York, N. Y.

Victor Chemical Works, Mt. Pleasant, Tenn.

Wagner Brothers, Inc., Detroit, Mich.

Western Electric Company, Inc., Chicago, Ill.

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Westinghouse Electric Corporation, E. Pittsburgh, Pa.

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